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RESEARCH INSTITUTE, NEW DELHI

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# COLLOID SYMPOSIUM MONOGRAPH

Papers and Discussions Presented at the  
**FIRST NATIONAL SYMPOSIUM ON COLLOID CHEMISTRY**  
University of Wisconsin, June, 1923

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Published by the Department of Chemistry  
University of Wisconsin, Madison  
1923



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The following papers and discussions were given at the First National American Symposium on Colloid Chemistry held at the University of Wisconsin June 12th to 15th, 1923.

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## FOREWORD

The amazing development of Colloid Chemistry and the realization of its tremendously important rôle in medicine, agriculture, and industrial processes have been the outstanding features of the present century, as far as chemistry is concerned. Each day brings new applications of colloid principles, and the underlying reasons for purely empirical procedure are gradually emerging from the haze of uncertainty and guess work. The theories of colloid behavior are constantly undergoing a process of evolution, a process of such rapid change that one can scarcely keep abreast of the tide, and the opportunities for frank and complete discussions of topics in which colloid chemists are interested have been inadequate.

During the past year, a number of researches in colloid chemistry have been carried out at the University of Wisconsin under the direction of Professor The Svedberg, of the University of Upsala. Lectures and seminaries have also been given in the subject. It seemed particularly fitting that a National Symposium on Colloid Chemistry be held while Professor Svedberg was in the country. Accordingly, such a symposium was held in Madison from June 12th to 15th inclusive, and many papers of fundamental importance and interest were read and discussed at length. In addition to the scientific program provided, ample opportunity was afforded for the colloid chemists to become better acquainted with each other. The University desires to express to the authors presenting papers its sincere appreciation of the coöperation which made this symposium an unusually profitable and interesting scientific meeting, in which the interest was sustained throughout the four-day period.

Grateful acknowledgment is hereby made to Professor Farrington Daniels, and Messrs. E. O. Kraemer, W. A. Koehler and M. H. Veazey for assistance in reading proof.

J. H. MATHEWS



[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY,  
UNIVERSITY OF WISCONSIN]

## THE HEAT OF COAGULATION OF SULFUR HYDROSOLS

FREDERICK L. BROWNE

Several years ago we began at Wisconsin a series of studies in the field of the thermochemistry of colloids. We were struck by the fact that while the earlier workers in colloid chemistry, for example Selmi, Graham, and Linder and Picton attached much significance to the absence of heat effects during the formation and coagulation of colloids, very little attention has been paid to this aspect of the question in these later days when the importance of colloid chemistry is so generally recognized. During the first twenty years of the present century, aside from some papers on heats of adsorption of gases and vapors by charcoal, silica, etc., and the heat of swelling of such materials as gelatin, the only publications concerning the heat effects during the formation and coagulation of colloids have been two brief papers by Doerinckel,<sup>1</sup> at Göttingen in 1910 and one by Kruyt and van der Spek,<sup>2</sup> at Utrecht in 1919 on the heats of coagulation of ferric oxide and arsenous sulfide hydrosols, chiefly, with electrolytes. Recently there has been a theoretical paper on the subject by Fricke.<sup>3</sup>

We felt that a more complete investigation of the thermal effects accompanying the formation and coagulation of colloids should throw new light on the question of the relations between colloidal dispersion and crystalloidal solution. The process of formation of crystalloidal solutions is always accompanied by heat effects, usually of considerable magnitude. Moreover, it is generally held that when not complicated by heats of solvation, ionization, hydrolysis, etc., the heat of solution is negative and is due to the separation of the molecules of the solute against the forces which hold them together in the crystal. If, then, crystalloidal solution and colloidal dispersion differ only in the dispersity of the particles, the process of coagulation would be expected to involve the evolution of heat.

<sup>1</sup> Doerinckel, *Z. anorg. Chem.*, **56**, 20; **67**, 161 (1910)

<sup>2</sup> Kruyt and van der Spek, *Kolloid-Z.*, **24**, 145 (1919)

<sup>3</sup> Fricke, *Z. phys. Chem.*, **101**, 185 (1922)



Kruyt and van der Spek found no measurable heat effect during the coagulation of arsenous sulfide hydrosol with potassium chloride and with aluminum sulfate, but with ferric oxide sol there was marked evolution of heat on coagulation with sodium sulfate. Doerinckel found similar results with ferric oxide and potassium oxalate or aluminum sulfate and with silicic acid and aluminum sulfate. Kruyt and van der Spek connect the difference in behavior with the suspensoid and emulsoid characters of the different sols.

On making a much more extended study of the heat of coagulation of ferric oxide hydrosol with electrolytes we<sup>4</sup> found that the heat effect accompanying coagulation varies very greatly with different electrolytes and particularly with the purity of the sol, that is to say, with the proportion of peptizing electrolyte present. At low purities the heat effect was large and might be either positive or negative depending upon the nature of the coagulating electrolyte and as the purity of the sol increased the heat effect became smaller until it fell within the limit of experimental error, namely about 1 or 2 calories per gram equivalent of ferric oxide.

This suggested that the observed heat effects might be due to the interaction of the electrolytes in the sol and in the coagulant. It was found, in fact, that on mixing the solutions used as coagulants with solutions of ferric chloride of different concentrations, after due allowance for the heats of dilution, heat effects of a similar order of magnitude were involved as in the coagulation of the sols.

Before the proper corrections could be applied for the heats of mixing of the electrolytes with the electrolytes already present in the sol it was necessary to obtain quantitative data as to the amounts of ferric chloride and hydrochloric acid present in the ferric oxide sols of different purity and concentration. For the purpose of these experiments sols prepared by Neidle's<sup>5</sup> method of oxidation of ferrous chloride solution with hydrogen peroxide and dialysis were selected because of their freedom from the ammonium chloride which is a by-product in the Graham method of preparation by addition of ammonium carbonate to ferric chloride solution.

<sup>4</sup> Browne and Mathews, *J. Am. Chem. Soc.*, **43**, 2336 (1921)

<sup>5</sup> Neidle, *ibid.*, **39**, 2334 (1917)

The method of procedure<sup>6</sup> consisted in measurements of the chloride ion activities in the ferric oxide sols and in ferric chloride solutions by means of the calomel electrode. Where possible the results were checked by measurements of hydrogen ion activities by means of the hydrogen electrode. It was found possible to use the hydrogen electrode in the presence of a certain amount of ferric ion by first saturating the electrode with hydrogen, plunging in the solution, and taking the potential at once.

The activity coefficient for chloride ion from ferric chloride was first determined from measurements in ferric chloride solutions containing enough nitric or sulfuric acid to minimize hydrolysis. Then by means of similar measurements in ferric chloride solutions containing no added acid the concentrations of hydrochloric acid and of ferric chloride in ferric chloride solutions of varying concentration were calculated and plotted against the chloride ion activities. Assuming, then, that ferric oxide sols consist of particles of hydrous ferric oxide with its adsorbed ions dispersed in a solution of ferric chloride, the measurement of the chloride ion activities gave the concentrations of ferric chloride and of hydrochloric acid in the dispersion medium. The sum of these two was always less than the total amount of chlorine in the sol, the difference representing the amount of chlorine compounds adsorbed by the ferric oxide.

It was found that below a purity of about 14, the purity being defined as the ratio of total iron to total chlorine in the sol, the dispersion medium contained both ferric chloride and hydrochloric acid, and the amount of hydrochloric acid checked very closely with the values for the hydrogen ion activity obtained with the hydrogen electrode. Above this purity the dispersion medium contains neither ferric ion nor hydrogen ion, but still contains notable amounts of chloride ion, in other words, the ferric oxide adsorbs the ferric and hydrogen ions completely, but not quite all the chloride ions. These observations also are checked by the behavior of the sol on dialysis.

Finally the heat of coagulation of these Neidle sols of varying purity with sodium sulfate solution was determined<sup>7</sup> and corrections applied for the heats of dilution of the sol and of the

<sup>6</sup> Browne, *J. Am. Soc. Chem.*, **45**, 297 (1923)

<sup>7</sup> Browne, *ibid.*, **45**, 311 (1923)

coagulant and for the heats of mixing of the sodium sulfate with the hydrochloric acid and the ferric chloride present. This gives the data of Table I.

TABLE I

## ANALYSIS OF THE HEAT OF COAGULATION OF FERRIC OXIDE HYDROSOLS

360 cc. of the sol containing 0.66 g. equiv. Fe per liter coagulated with 255 cc. 0.2 N sodium sulfate

Purity of sol	Heat of coagln. corrected for		H <sub>C</sub> Ht. of co- agln. per gm. eq. Fe cal.	H <sub>C</sub>	H <sub>C</sub>	H <sub>C</sub>
	Diln. cal.	Mixing cal.		Ad <sub>total</sub>	Ad <sub>Cl</sub>	Ad <sub>SO<sub>4</sub></sub>
4.44	-53.6	+47.4	+200	+1700	+1700	+4400
9.11	- 6.3	+47.7	+200	3100	1700	4400
13.0	+11.1	+51.1	+216	2700	2200	4800
17.1	+ 5.3	+35.3	+149	1700	1700	1800
27.2	+ 2.1	+22.1	+ 93	2700	2300	4900
47.5	0	+13.0	+ 55	3100	1700	4400
			Av.	2500	1900	4100

The first column gives the purity of the sol, the second the heat effect on coagulation corrected for the heats of dilution of the sol and of the coagulant, the third column the heat effect corrected also for the heats of mixing of the sodium sulfate with the ferric chloride and the hydrochloric acid in the sol, the fourth column this heat effect calculated per g. equiv. Fe in the sol. When the supernatant liquid after coagulation is analyzed for chloride and for sulfate it is found that some sulfate has been adsorbed and some chloride previously held by the ferric oxide given up. The values in the fourth column divided by the sum of these changes in ion adsorption give the figures in the fifth column. It will be seen that these values are reasonably constant at 2500 calories per g. equiv. change in adsorption. A better way to make the calculations is to take the data for the different sols in pairs and set up simultaneous equations with the heats of adsorption of sulfate and of chloride as unknowns and solve for these quantities. The values in the sixth and seventh columns were obtained in this way. It will be seen that the heat of adsorption of chloride ion under these conditions is about 1900 calories per g. equiv. chloride and the heat of adsorption of sulfate about 4100 calories.

The evidence seems conclusive that the heat effects observed

during coagulation of ferric oxide hydrosols with electrolytes are to be attributed entirely to the heats of dilution and of interaction of the electrolytes in the sol and in the coagulant and to the heat effects accompanying the changes in ion adsorption during the process. The change in dispersity of the ferric oxide from that characteristic of the sol to that of the coagulum does not involve a heat change measurable by our present methods. Moreover, Kruyt and van der Spek's suggestion that the heat effects with ferric oxide sols are due to its emulsoid characteristics is untenable. Either there is no change in hydration during coagulation or this change does not involve a heat effect.

It seemed desirable to extend these studies to other sols, particularly sols like ferric oxide which are considered to be highly hydrous. Sulfur hydrosols made by Odén's method are particularly interesting because of the possibility of separating them by fractional coagulation with sodium chloride into sols having large and small particles.

The sols were prepared by the directions given by Svedberg.<sup>8</sup> 350 g. concentrated sulfuric acid was placed in a beaker surrounded by ice-salt mixture and stirred vigorously by a mechanical stirrer while 250 g. of sodium thiosulfate dissolved in 150 g. of water was added so slowly that the temperature of the mixture did not rise above 25°C. These are the optimum conditions for obtaining a large yield of colloidal sulfur. 150 g. of water was then added, the mixture warmed to about 80° and filtered to remove coarse sulfur. The sol was then completely coagulated by adding sodium chloride and the residue separated by filtration. This was redissolved in water. This process of coagulation and reprecipitation was repeated seven times. The sol was finally peptized in distilled water and dialyzed in collodion sacks against distilled water for three days to remove sodium chloride. Numerous batches made in this way were combined to give one large batch of sol containing 14.8 g. of sulfur per liter. This will be known as sol 30.

A part of sol 30 was treated with sodium chloride until the concentration of the latter was 0.15 *N*. This caused the precipitation of approximately half the sulfur, the portion coming down consisting of the coarser particles. These were removed

<sup>8</sup> Svedberg, *Kolloid-Z.*, **4**, 50 (1909)

by filtration and reprecipitated in distilled water, yielding sol 31. The remainder of sol 30 was treated with more sodium chloride until all the sulfur was coagulated. This was filtered off and reprecipitated in distilled water, giving sol 32. These sols were diluted until they contained 14.8 g. of sulfur per liter, and enough sodium chloride was added to sol 31 so that it contained the same amount as sol 32. The sodium chloride content of sol 30 was considerably less because of its purification by dialysis.

Some slight modifications of the calorimeter previously described were made to permit the use of smaller samples of the sol, 200 cc., and of the coagulant, 10 cc. The sol was contained in a silver can supported on cork legs in a larger silver can contained in the calorimeter vessel. The calorimeter vessel was closed by a cover, clamped on with a rubber gasket to make a water tight joint, provided with the necessary tubes through which the stirrers, thermometers, etc., passed. The whole was placed in a water-bath the temperature of which could be altered at will by means of an electric heater or addition of ice water. A thermocouple with one arm in the outer bath and the other in the calorimeter contents enabled us to keep the outer temperature properly adjusted to hold that inside constant before and after mixing of the solutions. The calorimeter temperature was measured with a platinum resistance thermometer reading to  $0.0001^{\circ}$ . The 10 cc. of coagulant was held in a small conical vessel closed at the bottom with a rubber stopper so arranged that it could be pushed out at the proper moment.

With sodium chloride the sol was not completely coagulated at a concentration of  $0.29 N$  and the heat of coagulation amounted to 16.7 calories per g. equiv. S. At a concentration of  $0.57 N$  sodium chloride the sol was completely coagulated and the heat effect was slightly less, 16.2. It is the very smallest particles of sulfur that failed to coagulate in the first case, consequently one would expect the value for the heat effect in the second case to be notably larger than in the first if the heat effects were due to the change in dispersity of the sulfur particles during coagulation.

The electrolytes used as coagulants include sodium, potassium, magnesium, and aluminum chlorides. The heat

effects on coagulating 200 cc. of the sol with 10 cc. of the coagulant were corrected for the heat of dilution of the coagulant (the heat of dilution of the sol was zero) and are shown in Table II.

TABLE II  
HEAT OF COAGULATION OF SOL 30 WITH VARIOUS ELECTROLYTES

200 cc. sol 30 containing 0.185 g. equiv. S coagulated with 10 cc. of electrolyte solution

Coagulant	Concn. of coagnt. in final mixture, g. equiv. per l.	Corrected heat of coagulation, cal. per g. equiv. S.	Remarks
Sodium chloride	0.29	16.7	Not completely coagulated
“ “	0.57	16.2	Completely coagulated
Potassium chloride	0.168	88.6	“ “
Magnesium chloride	0.342	-20.5	“ “
Aluminum chloride	0.169	-20.3	“ “
“ “	0.085	-9.3	“ “
“ “	0.042	-3.1	“ “
“ “	0.021	0.0	“ “
“ “	0.0105	0.0	Nearly all coagulated

With potassium chloride at 0.168 *N* the heat of coagulation was found to be 88.6 calories per g. equiv. S. With magnesium and aluminum chlorides, however, the heat effects are always negative. With aluminum chloride, as the concentration of the coagulant decreases the heat effect rapidly becomes less until below 0.021 *N* it is not detectable, although coagulation of the sol is complete.

The great variation in the heat effects from + 88.6 calories in the case of potassium chloride to -20.5 calories with magnesium chloride, and the marked dependence upon the concentration of the electrolyte shown by aluminum chloride indicate that these heat effects must be attributed to something other than the change in dispersity of the sol during the coagulation. Since sulfur sols are known to contain significant amounts of polythionic acids which are necessary for their stability it seems evident that we are dealing with phenomena similar to those involved in the case of ferric oxide sols, namely, the heats of mixing of the coagulants with the polythionic acids in the sols and the heat effects accompanying changes in the ion adsorption.

Table III gives the heats of coagulation observed with 0.021 *N* aluminum chloride and sols 30, 31, and 32. The sulfur particles in sol 31 were those which are thrown down in 0.15 *N* sodium chloride, consequently according to Odén<sup>9</sup> are over about 30  $\mu\mu$  in diameter. Those in sol 32 were under this limit. It will be seen that the heat of coagulation with 0.021 *N* aluminum chloride is less than the limits of experimental error, about 0.2 or 0.3 calorie per g. equiv. S. Even with the very small colloid particles of sol 32, therefore, the average size of which is considerably less than 30  $\mu\mu$ , there is no evidence of any heat effect accompanying the change in dispersity during coagulation or any change in hydration which may be involved in this change. This is good evidence also that the sulfur in the coagulum is in the same allotropic state as it exists in the sol.

TABLE III  
HEAT OF COAGULATION OF SOLS OF VARYING PARTICLE SIZE

Sol	Size of particles	Heat of coagulation
30	All sizes	0.0 cal.
31	Over 30 $\mu\mu$	-0.1
32	Under 30 $\mu\mu$	-0.1

#### DISCUSSION ON F. L. BROWNE'S PAPER THE HEAT OF COAGULATION OF SULFUR HYDROSOLS

R. THIESSEN: Are sulfur particles negatively charged?

F. L. BROWNE: Yes.

T. SVEDBERG: I think that this investigation by Dr. Browne is very important as well as interesting, and will add to our better understanding of the coagulation process. It may be that the coagulation actually involves a change in the degree of dispersion. At the present time we are inclined to think that at least in the first stage there is merely an aggregation of the particles and it is quite obvious that with such an aggregation of particles one would not expect any great heat effect. This paper seems to confirm this view. Especially in the case of sulfur sols it is known that the number of particles is absolutely constant, after coagulation and peptization again,

<sup>9</sup> Odén, *Z. physik. Chem.*, **78**, 682 (1912)

especially in such case it is very interesting to see that there is practically no heat effect at all. It only means a rearrangement of the particles, not a real change of dispersity.

Of course after the preliminary aggregation during the coagulation there may be in many cases a change in dispersity or coalescence of the particles taking place more slowly. I think it would be of interest to carry out some experiments to see if there is a heat effect accompanying this process. Of course it would be very difficult because the process is so slow.

H. N. HOLMES: I was very much interested in what Dr. Svedberg has just said, because a few years ago I studied the amount of ferric chloride required to peptize ferric arsenate which had been freshly precipitated or precipitated and allowed to age for varying lengths of time. It was found that for the peptization of the very freshly precipitated material it required a certain amount of ferric chloride, and in a few minutes it took more ferric chloride, and in half an hour decidedly more, and up to twenty-four hours the amount of ferric chloride required increased, and then after twenty-four hours there was very little change. This rapid rise in the curve during the first twenty-four hours was significant. It convinced me that there was a steady physical change taking place during that time. At first no doubt we had an aggregation of the primary particles, and then some sort of a coalescence, and then dehydration. These changes may be accompanied by heat effects. Of course I did not follow it up with that view in mind, but it might possibly have been worth looking into. I was looking at it from the standpoint of peptization. As we squeeze out the water in precipitated ferric oxide the ability of the mass to peptize again in ferric chloride becomes less and less, and in the ability of acids to dissolve certain precipitates we know that a change takes place on ageing. All this has a relation to the paper in question.

R. E. WILSON: I would like to ask Dr. Holmes whether the characteristics of those sols after re-peptization seemed the same?

H. N. HOLMES: I don't know; I was just measuring this change in peptizing.

R. E. WILSON: Was there any difference in appearance?

H. N. HOLMES: Not any striking difference. It didn't catch



my eye at all, but to carry it back and forth might have been well worth while doing.

J. ALEXANDER: Have you made any experiments with colloidal metals?

H. N. HOLMES: No.

J. ALEXANDER: If my recollection is right, Prange reported a large heat effect during the coagulation of colloidal silver with electrolytes, and a further evolution of heat when the amorphous precipitate was converted to crystalline silver by treatment with dilute acids.

F. L. BROWNE: But in those experiments of Prange the silver sol was prepared by the Carey Lea method and was not dialyzed, so it contained large ~~amounts of electrolytes~~. Hence there were so many possibilities for heats of ~~reaction~~ between the electrolytes and the coagulant that it seems to me that his conclusions are not very valuable.

J. ALEXANDER: I do not remember whether Prange made the proper corrections.

F. L. BROWNE: I do not think he made any corrections except for heats of dilution of the coagulant. In connection with Dr. Wilson's question, I should like to say that we prepared ferric oxide sols by several different methods including addition of ammonium carbonate to ferric chloride, addition of HCl to ferric oxide sol of high purity, and peptization of precipitated and washed ferric oxide in ferric chloride, and in all cases the heat of coagulation for a sol of given purity was the same. This seems to indicate that, although the ease with which ferric oxide can be peptized by ferric chloride varies greatly with the age of the precipitate, etc., the sol which results on peptization in a given amount of ferric chloride, is always the same.

F. E. E. GERMANN: I was just wondering, wouldn't it be better to use a vacuum bottle for the calorimeter and keep the surroundings at constant temperature by means of cracked ice.

With the apparatus employed we have to keep heating or cooling the water in the outer bath because we find it varying so much, whereas if we use our vacuum bottle apparatus we obviate that, inasmuch as ice keeps a steady temperature. We could follow these small temperature changes far more accurately if we had the vacuum bottle in the ice bath and

applied the correction for radiation after the coagulation took place.

F. L. BROWNE: (Explained in detail the method of operation of the calorimeter used. See *J. Am. Chem. Soc.*, **43**, 2336 (1921)).

R. A. GORTNER: Undoubtedly during the coagulation of sols there is a secondary change following the preliminary aggregation of the particles. I have been playing a good deal with gold sols, following the individual particles during coagulation with the ultramicroscope. In working with a gold sol, you can see around the gold particles a halo which is probably the water film. At first on coagulation the particles come close together so that the halos touch, and the original particles, with their halos, can still be seen in the aggregates. Then you will see that the halos disappear around the individual particles and the gold particles themselves seem to touch.

In this secondary change the mass of gold particles becomes more compact and the water film about them becomes smaller in area. This secondary change does not take place until some time after the coagulation.

A. R. JOHNSON: I would like to ask about the specific heat of the ferric oxide and sulfur sols. In 1912 Mr. Hammer did some work on the specific heat of milk and found that the specific heat appeared to be different before and after it was coagulated. The question that arose in our minds was this: Is the specific heat of a system in which we have colloids the same before precipitation as after?

F. L. BROWNE: We didn't determine the specific heats. Instead of that our general procedure was to carry out the coagulation as I have described, then after the temperature had again become constant, we passed a measured amount of electrical energy through a resistance coil submerged in the calorimeter contents and measured the resulting rise in temperature. In that way we obtained the amount of energy required to raise the calorimeter and its contents through one degree of temperature. Then multiplying that by the temperature change observed during the coagulation, we obtained the energy change during coagulation. In that way we avoided the necessity of determining the specific heats and water equivalent of the calorimeter.

A. R. JOHNSON: Do you know whether the specific heat is

the same for colloids before precipitation and after precipitation?

F. L. BROWNE: No, we haven't determined that.

H. S. TAYLOR: If the heat of coagulation is zero, what brings the particles together? Has Dr. Browne a theory of coagulation to present? I wondered if the method of computing the heat of coagulation whereby the heats of adsorption are subtracted, bringing the heat effect to zero does not actually cut out the energy change which is involved in the coagulation process. May it not be that the coagulation is caused by the adsorption of the electrolyte on the particles of the colloid, and that the actual coagulation consists in the multiplication of colloid particles attached to a single adsorbed ion? May it not be that the coagulation of the particles is due to adsorption of sodium sulphate by two or more particles of colloid, and that in subtracting the heat of adsorption you are actually eliminating the thing which causes the coagulation?

F. L. BROWNE: In that case we would have to consider, would we not, that the size of the individual particles in ferric oxide sols of different purities would be vastly different in view of the difference in the amounts of sodium sulfate required for coagulation and the relative amounts of ferric chloride causing their stability. That is, the size of the particles in the sol having a purity of 47.5 would be very much larger than in the case of a sol with a purity of 4. In the case of ferric oxide I do not think that we have any definite evidence as to what the size of the particles is. In the microscopic field all you can see is a Tyndall cone with sols of all purities. I am not prepared to say whether there is any very great difference in the dispersity at the higher and the lower purities. Personally I rather feel that the difference in the size of particles is not as great as the difference in the relative amounts of peptizing electrolytes and ferric oxide present or in the amounts of sodium sulfate required for coagulation.

T. SVEDBERG: In the case of sulfur sols the amount of adsorbed sodium chloride was calculated by Gustaver recently from Odén's data. The amount of sodium chloride per unit of surface was the same for different sized particles. He showed that approximately a molecular layer of salt covers the surface of the particles. Of course the change in the

concentration of electrolytes in the surface field of the particle must be accompanied by some change of heat effect. But what I emphasize, and which is an interesting factor, is that the coagulation itself, that is, the aggregating together of the particles, does not involve any heat change. This fact is really important because in many textbooks we find the view expressed that coagulation indicates change in specific surface. That is probably not the case here.

## PRECIPITATION OF SOLS BY ALCOHOL

BY WILDER D. BANCROFT

According to Billitzer<sup>1</sup> platinum is charged negatively in water and positively in alcohol, the reversal occurring at about seventy-five per cent. alcohol by volume. This means that a colloidal solution of platinum would be precipitated by the addition of sufficient alcohol. There seems to be no special reason why the effect of alcohol on platinum should be specific and we therefore conclude that alcohol tends to precipitate negatively charged sols. The actual precipitation may depend on the presence of salts which bring the colloid nearer to the iso-electric point, thus making the sol less stable.

The negatively charged globules in rubber latex can be precipitated by alcohol in presence of salts.<sup>2</sup> Thaer<sup>3</sup> states that negatively charged humus is precipitated by alcohol if the concentration of electrolytes is not too low, while van Bemmelen<sup>4</sup> found that alcohol peptizes humus when the latter is charged positively by the addition of acid. Rona and Gyorgy<sup>5</sup> state that the rate of sedimentation of negatively charged kaolin is increased by the addition of alcohol, while Klein<sup>6</sup> has some rather unsatisfactory experiments to show partial agglomeration by alcohols of negatively charged arsenic sulphide, gold, silica, and ferric oxide, while no agglomeration was obtained with positively charged ferric oxide and alumina. It seems probable that more striking results would have been obtained if salts had been added instead of relying upon the alcohols to cause precipitation. As a matter of fact Klein used amyl alcohol dissolved in ethyl alcohol and considered that the ethyl alcohol did nothing more than make the amyl alcohol partially miscible with water.

If we assume, as seems justified, that one effect of adding alcohol to a hydrosol is to destabilize a negatively charged sol,

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<sup>1</sup> *Drude's Ann.*, 11, 902; *Z. physik. Chem.*, 45, 312 (1903)

<sup>2</sup> Hübener, *Kolloid-Z.*, 16, 7 (1915)

<sup>3</sup> *Göttingen Dissertation*, 1910, 109

<sup>4</sup> Ehrenberg, "Die Bodenkolloide," 1915, 57

<sup>5</sup> *Biochem. Z.*, 105, 133 (1920)

<sup>6</sup> *Kolloid-Z.*, 29, 247 (1921)

there are several interesting corollaries. Suppose we make up a cell with silver electrodes and dilute silver nitrate of the same composition in water and in aqueous alcohol. The alcohol will probably not force back the dissociation of the silver nitrate appreciably and, if it did, would make the alcoholic solution anodic. If the alcohol decreases the negative charge on the silver, it will make the alcoholic solution cathodic. Actually, this is what happens. Jones<sup>7</sup> has made a number of experiments of this sort and reports that the alcoholic solutions are always positive relatively to the aqueous solutions. He was not using aqueous alcohol but diluting the alcohol would give intermediate values and he was getting electromotive forces of the order of one-tenth of a volt. A correction for a decreased dissociation of silver nitrate in alcohol would increase this value. Jones draws the conclusion, very properly, that the solution pressure of metals varies with the solvent, the phrase "thermodynamic environment" not having been invented at that time.

We now see that the effect is due in great part to adsorption of alcohol. Since we can also bring sols to the iso-electric point by adding suitable electrolytes, this means that we can change the so-called solution pressure in this way. Suppose we have a silver electrode in a dilute silver nitrate solution and add an electrolyte which does not react with silver nitrate and which has one ion that is adsorbed very strongly by silver. If this is the cation it will make the silver more positive, and if it is the anion it will make the silver more negative. In other words the potential difference of a reversible metallic electrode is not determined solely by the concentration of the metallic ion; but may vary with the nature of the other ions in the solution. The effect is likely to be relatively large in the case of complex salts where the concentration of the metal salts is low and that of the other ion is high. This means that practically all our calculation of ion concentrations from electromotive-force measurements must be revised. The experiments of Burton<sup>8</sup> on the effect of salts on colloidal solutions of metals are distinctly interesting though he did not have a constant concentration of the metal ions and consequently

<sup>7</sup> *Z. physik. Chem.*, **14**, 352 (1894)

<sup>8</sup> *Phil. Mag.*, [6] **17**, 583 (1909)

his results may be due in part to a changing concentration of the metal ions.

We know that silver bromide forms a positively charged sol in presence of a slight excess of a silver salt and a negatively charged sol in presence of a suitable amount of a soluble bromide. There seems no reason for postulating that negatively charged silver bromide has the same solution pressure as positively charged silver bromide. If the two are different, all our formulas for change of solubility on adding another salt will have to be revised.

Our formulas for electromotive forces and for solubility changes are deduced on the implicit assumption that there is no adsorption and consequently are in error to some extent. Whether this error is an appreciable one in most cases remains to be seen; but we do know that the failure of the flowing electrode to give us true single potential differences is due to adsorption. Most of us have assumed that we knew the single potential difference to within a tenth of a volt; but the experiments of Billitzer, recently confirmed by Garrison,<sup>9</sup> indicate that the error may be of the magnitude of 0.7 volt. However this may be, it is quite evident that the orthodox physical chemistry must be modified so as to take account of effects due to adsorption.

CORNELL UNIVERSITY

#### DISCUSSION ON W. D. BANCROFT'S PAPER PRECIPITATION OF SOLS BY ALCOHOL

T. SVEDBERG: The difficulties in determining potential differences were pointed out by Dr. Bancroft, but the problem is of considerable importance. However, I am not of the opinion that we are justified in coming to the conclusion that we do not know the actual value of the absolute potential difference to 0.7 of a volt. But in regard to Garrison's recent determination, I think that quite the same objections can be raised against his experiments as against the experiments made by Billitzer. The only difference is that the particles used by Garrison are much larger. He observed the movement of a silver needle immersed in a solution of a silver salt. Such

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<sup>9</sup> *J. Am. Chem. Soc.*, **45**, 37 (1923)

a method involves the same principle as that underlying Billitzer's experiments. Some workers have shown that the potential difference between the interior of a solid and of a liquid bathing it is not coincident with the potential difference as determined by the Nernst theory.

Smoluchowski suggested that the measurement of the potential difference at solid-liquid interface based upon electrokinetic phenomena gives the difference of potential between a point in the absorbed liquid layer and the interior of the liquid, while the measurement of the ordinary electrode potential gives the potential difference between interior of solid and interior of liquid in accordance with Nernst's theory. These two potential differences are independent of each other.

The difficulty in measuring the absolute potential by means of the capillary electrode, where according to Helmholtz' theory the zero potential difference corresponds to a maximum of surface tension, is largely being overcome by recent experiments.



## GEL FORMATION

BY HARRY N. HOLMES

When a substance is formed in a liquid in which it is insoluble or when conditions attending a substance in solution are so changed as to decrease greatly its solubility, a precipitate is formed, crystalline or amorphous as the case may be.

When the precipitated substance holds much of the liquid in a more or less solid mass it is referred to as a "gel" or as a "gelatinous precipitate." A gel or, as it is often termed, a "jelly" usually holds all the liquid at first although free liquid may separate later. In any event the gel has greater rigidity and elasticity than the gelatinous precipitate. Gel structure is more uniform. However, any distinction between the two is rather arbitrary.

1. GEL FORMATION BY COOLING.—This is the simplest method of gel formation—and the best known. When a 2 per cent. solution (or dispersion) of agar in hot water is cooled the whole of the water is held by the agar in a very stiff gel. Gelatin gels of very low concentration are prepared in the same way. Similarly a soap gel develops on cooling hot soap solutions, or dispersions, of the proper concentration. Sodium stearate gels, solid at room temperature, have been made with 0.5 per cent. soap and 99.5 per cent. water.

It seems probable that on cooling these sols the molecules or smaller aggregates unite to form long filaments which interlace in a sort of "brush-heap" structure. This alone could account for the entangling of much water in the capillary spaces between fibers. However, it is more probable that in the gels of best structure the aggregates of gelatin or other material are hydrated by adsorption of water thus greatly thickening the filaments. Much water not actually adsorbed could then be held by capillary action. In some instances water may even dissolve in the aggregates.

Some distinction should be made between "true gels" of the agar, soap or gelatin type where the interlacing fibers undoubtedly adsorb much water (or other liquid) and the "false gels" of the caffeine type in which interlacing needle-like crystals

entangle considerable water without actually adsorbing it on the surfaces of the caffeine crystals. This distinction is shown by dissolving 4-5 g. of caffeine in 100 cc. of boiling water and then allowing the solution to cool overnight. The beaker may be inverted without loss of water yet close examination reveals a structure of comparatively coarse crystalline needles. On stirring, the water is released due to the breaking down of the network. Cold water can hold only about 2 per cent. caffeine in solution while boiling water dissolves a little more than 4 per cent.

Of course there must be gels of every gradation in between the two extremes given above. The degree of adsorption of the liquid, the solubility of the liquid in the solid and the fineness and length of the crystals or filaments must have much to do with the structure of gels. It is, perhaps, not sufficiently exact to speak of the water (or other liquid) as adsorbed. It may really dissolve in the filaments thus swelling them greatly. Martin H. Fischer believes that at higher temperatures we have solutions or dispersions of soap-in-water; at lower temperatures of water-in-soap; and between these extremes various mixtures.

2. GEL FORMATION BY DOUBLE DECOMPOSITION.—A very familiar illustration of this method is the preparation of a silicic acid gel by addition of an acid to a sodium silicate solution in proper concentrations. In this case the silica must be regarded as very highly hydrated as one mole of silica in a fresh gel may hold 300 mols of water. Using X-ray interference methods Scherrer failed to find any trace of crystalline structure in silicic acid gels although such structure began to appear on drying or ignition.

Reaction probably quickly follows mixing of acid and water-glass solutions. Yet the solutions may be so selected that the liquid mixture will "set" to a solid gel after one month. This means that hydration is slow in the presence of certain ions or that the silica molecules are slowly forming chains analogous to carbon chains in the organic world. On dialysis of such a fresh mixture much silica passes through the membrane although after a time this ceases. Unquestionably molecules of silica or silicic acid are first formed. If these grew by hydration in a roughly spherical way the aggregates would touch like oranges close packed in a box when the spheres occupy about

74 per cent. of the total volume. Of course this is true for uniform spheres only but it will hold in this case as an approximation. On further growth flattening of spheres and development of a solid would result. On the other hand if it be argued that the silica molecules develop into polysilicic acids a filamentous structure would result with adsorbed and capillary held water.

Victor Lenher<sup>1</sup> applied pressures up to 300 tons per square inch and squeezed out most of the water from such gels. The product obtained showed a water content of 12.3 to 12.9 per cent., which closely approximates the ratio of one molecule of water to two of silica.

Von Weimarn made precipitates of barium sulfate, sodium chloride, silver chloride and similar substances of degrees of dispersion ranging all the way from coarse crystalline precipitates to gelatinous precipitates and thick transparent colloidal gels. He held that any very difficultly soluble salt will separate as a gel if made by mixing sufficiently concentrated solutions.

It is essential that enough of the salt be precipitated in a medium in which its solubility is slight in order to produce suddenly a very high degree of supersaturation. This slight solubility may be secured in some cases by addition of considerable alcohol to the aqueous solutions.

Degree of dispersion of a precipitate and degree of supersaturation are closely related. Von Weimarn himself considered his best transparent gels as made up of ultra-microscopic crystals. Many of his products should be classed as "false gels" while others of "true gel" structure doubtless contained a network of ultramicroscopic crystals more or less hydrated.

When von Weimarn mixed solutions of  $\text{Ba}(\text{CNS})_2$  and  $\text{MnSO}_4$  at concentrations ranging from  $N/7000$  to  $N/600$  the precipitate was thrown down as a fine powder which, under the microscope was seen to consist of distinct individual crystals. But when the solutions were mixed at concentrations ranging from  $0.75 N$  to  $3 N$  the precipitate varied from granular to gelatinous. The most gelatinous showed no crystals under the microscope. In this instance the degree of supersaturation suddenly achieved was relatively great.

<sup>1</sup> *J. Am. Chem. Soc.*, **43**, 391 (1921)

3. GEL FORMATION BY ADDITION OF A COAGULATING LIQUID.—On the addition of considerable alcohol to an aqueous solution of pectin a transparent gel is formed. Similarly when chloroform is mixed with a dispersion of cellulose nitrate in amyl acetate a clear gelatinous mass is formed. However, on pressing this mass between the fingers nearly all of the liquid is squeezed out and a mesh of nearly dry cotton fiber is all that remains. Evidently most of this liquid was held in coarse capillary spaces.

4. GEL FORMATION BY ADDITION OF COAGULATING IONS.—In many colloidal sols the dispersed particles are kept from coalescing by the repellent effect of adsorbed negative ions in the case of a negative sol or of positive ions in the case of a positive colloid. Obviously neutralization of these ionic charges may permit coagulation. This may be secured by addition of just enough of a negative ion to a positive sol, for example, or of a positive ion to a negative sol.

Under such conditions substances which, like  $\text{As}_2\text{S}_3$ , are but slightly hydrated do not form gels nor even gelatinous precipitates. Even highly hydrated substances may fail to form a gel if precipitation is too rapid. The time element is important in securing the regularity of structure peculiar to a gel.

Weiser<sup>2</sup> prepared a beautiful green gel of hydrous chromic oxide containing 85 liters of water to one mol of  $\text{Cr}_2\text{O}_3$ . Starting with the positive sol, hydrous chromic oxide, he added just enough potassium chromate to cause coagulation in an hour or two. Here the divalent negative chromate ion was effective. Addition of too little chromate caused incomplete precipitation while too much gave only a gelatinous precipitate.

5. GEL FORMATION BY DIALYSIS.—An effect opposite to that mentioned in the preceding paragraph may be secured by removal of peptizing ions. Dialysis offers the best means of slowly removing such ions.

"Although at first some ferric chloride was found in the dialysates later only hydrochloric acid passed through the membrane. It was evident that gel formation depended on the slow removal of the acid derived from the hydrolysis of ferric chloride. In fact, when the ferric arsenate precipitate was peptized by

<sup>2</sup> *J. Phys. Chem.*, **26**, 430 (1922)

barely enough ferric chloride rather than by a decided excess, the gel formed more quickly and was not as clear nor of so good a texture. The small amount of hydrochloric acid developed was dialyzed out too rapidly to insure the best gel structure. Without question the time element is of prime importance."

Grimaux<sup>3</sup> observed that when precipitated ferric arsenate was peptized by ferric chloride and the sol dialyzed, a clear red gel resulted. Holmes and Rindfusz,<sup>4</sup> Holmes and Arnold,<sup>5</sup> and Holmes and Fall<sup>6</sup> extended this work.

It was reasoned by Holmes and Fall, from whose paper in 1919 the above paragraph was quoted, that slow addition of any base must, of course, neutralize the hydrochloric acid and thus remove the hydrogen ion as effectually as is done in dialysis. Quick addition of a base produced mere gelatinous precipitates.

To stress the time element these authors placed 2 cc. of *N* ammonium hydroxide on one side of a membrane and 10 cc. of ferric arsenate sol on the other side. In a week a beautiful, clear gel resulted. The base dialyzed slowly into the colloid neutralizing the hydrochloric acid at a rate permitting the formation and hydration of the ferric arsenate into a good gel structure. Even the dialysis of 2 cc. of a saturated solution of sodium acetate against 50 cc. of ferric arsenate sol produced a firm, clear gel in one week. Here the sodium acetate slowly repressed the ionization of the hydrochloric acid and, for gel-forming purposes, did the same work as the base.

6. EMULSION GELS.—It is generally held that in emulsions there is a concentration of emulsifying agent at the interface between dispersed and continuous phases. When the drops of dispersed phase occupy more than 74 per cent. of the total volume there must be some flattening of drops. Thus concentration layers around the drops would be forced into a honeycomb structure giving considerable body and rigidity to the system.

A 75 per cent. emulsion of kerosene dispersed in water containing 0.4 per cent. of gelatin becomes so solid on standing a

<sup>3</sup> *Compt. rend.*, 98, 1540 (1884)

<sup>4</sup> *J. Am. Chem. Soc.*, 38, 1970 (1916)

<sup>5</sup> *Ibid.*, 40, 1014 (1918)

<sup>6</sup> *Ibid.* 41, 763 (1919)

short time that a 3 cm. tube of the emulsion can be inverted without ready flow.

A more beautiful example of emulsion gels is found in the chromatic emulsions of Holmes and Cameron.<sup>7</sup> Glycerol is dispersed in an amyl acetate solution of a certain cellulose nitrate (as the emulsifying agent). The resulting milky emulsion is rendered transparent by addition of enough benzene to make indices of refraction of the two phases equal. The benzene mixes with the amyl acetate but not with glycerol. Although not pertinent to the topic in hand it is interesting to note that proper additions of benzene with its high optical dispersive power give all the colors of the rainbow to the emulsion. Such emulsions "cream" downward, the cream being rich in heavy glycerol. This beautifully colored cream soon stiffens to a gel which quivers when shaken. Here the honey-comb structure is due to the adsorption films of cellulose nitrate. When carbon disulfide is used instead of benzene the emulsions, although more beautiful, do not cream so readily. Since much less carbon disulfide is used to bring out the colors the creams, when formed, are not gels but merely very viscous liquids.

In all the previously discussed methods of gel formation care must be taken not to stir the liquid while gel structure is developing. Otherwise a lumpy or buttery mass results.

#### SPECIAL GELS

**DI-BENZOYL CYSTINE GEL.**—Theories of gel structure must take into account the remarkable di-benzoyl cystine gel recently prepared by R. A. Gortner and W. F. Hoffman. Brenzinger<sup>8</sup> was the first to study this gel. Gortner's method of preparation is to dissolve 0.2 g. of pure di-benzoyl cystine in 5 cc. of hot 95 per cent. alcohol. He adds hot water slowly (keeping the solution boiling) to a volume of 100 cc. On cooling a transparent gel, as rigid as 5 per cent. gelatin, is formed after a few hours. In time opaque nuclei of stellate groups of needles appear. This gel is 99.8 per cent. water and yet is a solid.

**CALCIUM ACETATE GEL.**—A few years ago Baskerville

<sup>7</sup> *J. Am. Chem. Soc.*, **44**, 71 (1922)

<sup>8</sup> *Z. physiol. Chem.*, **16**, 1537 (1892)

patented a process of making "solid alcohol" illustrated by quick mixing of about 85 cc. of 95 per cent. alcohol with 15 cc. of a saturated aqueous solution of calcium acetate. A very firm gel sets instantly. The alcohol must act as a dehydrating agent. Probably both liquids are adsorbed by the very minute crystals. Von Weimarn would doubtless point to this as the sudden development of a very high degree of supersaturation by addition of alcohol. On standing several hours such a gel synerizes and shows a great many small white pellets settling from a clear liquid. Under the microscope these pellets are seen to be stellate groups of needle crystals. Acetone may be substituted for alcohol with success.

**SOAP GELS.**—Martin H. Fischer in his book, "Soaps and Proteins," presents a large amount of important information on soap gels. On cooling hot water dispersions of certain soaps in proper concentration solid gels result. The amount of water held in such solid form varies with the type of soap. The soaps derived from saturated fatty acids are much more highly hydrated than those derived from unsaturated fatty acids. Hence soaps made from liquid fats hold less water than soaps made from solid fats.

1 mol sodium laurate holds	4 liters water	} Saturated
1 " " stearate " 37 " "		
1 " " oleate " 1 " "		} Unsaturated
1 " " linoleate " 1 " "		

The heavier the fatty acid molecule the more highly hydrated the soap. Such soaps are also more highly alcoholated for it should be noted that soap gels are possible with other liquids than water. With the more complex alcohols, a given soap holds more in the solid gel form.

A 0.5 per cent. solution of sodium oleate in very hot "Veedol" or "Arctic" oils (commercial lubricants) sets to a clear gel on cooling. This is interesting because there are no ions present. Consequently ionic theories of gel structure must take this gel into account. In aqueous systems certain ions have a marked influence on structure but they are not essential in all cases.

**HATSCHEK'S GEL.**—Hatschek<sup>9</sup> found that a 5 per cent. solution of camphorylphenylthiosemicarbazide in boiling alcohol, cooled slowly, developed crystals but, cooled rapidly, turned

into a clear gel. On long standing crystal rosettes appeared in the gel and at last the gel structure disappeared leaving only crystal rosettes in a clear saturated solution.

When a 5 per cent. solution in boiling carbon tetrachloride was poured into enough warm liquid paraffin to make the final concentration 1 in 350 the mixture set, on cooling, to a gel clear as glass.

**DOHLE'S GEL.**—Dohle<sup>10</sup> prepared a potassium salt of sulfonated benzothiazolmethensulfide. When he mixed a solution of this salt (at from  $N/5$  to  $N/100$ ) with equivalent quantities of a mercuric chloride solution a stiff gel resulted in a few hours. On standing this hydrolized to a crystalline basic salt.

**CERIC HYDROXIDE GEL.**—A. Müller dialyzed an 11 per cent. solution of ceric ammonium nitrate four days. On addition of extremely minute quantities of electrolytes to the clear yellow sol it set to a clear gel. Yet if the sol were heated 30 minutes at  $100^{\circ}$  the addition of electrolytes gave no gel but only a gelatinous precipitate.

**HYDROUS NICKEL OXIDE GEL.**—Tower<sup>11</sup> and Cooke dissolved nickel acetate in glycerol to which they added an alcoholic solution of potassium hydroxide. A green gel formed in a few minutes but when aqueous potassium hydroxide was used a gelatinous precipitate resulted.

On standing the gel synerized to a green sol with complete disappearance of the gel. Dialysis of this sol (with slow removal of potassium hydroxide) developed the gel structure once more.

**PECTIN GELS.**—The usual fruit jelly is made from fruits containing acid and pectin to which are added water and sugar. Such a gel may be made without the fruit if 1 g. of pectin (prepared easily from white rind of grape fruit) 0.5 g. of tartaric acid and 60 g. of sugar are boiled in 100 cc. of water until the mixture boils at  $103^{\circ}$ . Achieving this boiling point is merely a device to secure the proper concentration.

Pectin dispersed in water (by heating) may be thrown out as a clear gel by addition of alcohol. Even a saturated solution of calcium chloride will do this, as will an equal volume of

<sup>10</sup> *Kolloid-Z.*, **12**, 71 (1913)

<sup>11</sup> *J. Phys. Chem.*, **26**, 733 (1922)



glycerol. Without doubt these substances act as dehydrating agents thus concentrating the pectin sol. Were the pectin not hydrated it would, doubtless, be thrown out as an ordinary precipitate.

A pectin sol is readily coagulated by lead or copper salts yet, if a saturated solution of one of these salts is placed on one side of a dialyzing membrane and a pectin sol on the other, a gel is formed. This is another illustration of the importance of slow diffusion, the time element, in gel formation.

**SILICIC ACID GELS.**—In a paper<sup>12</sup> on "Silicic Acid Gels," I outlined methods of preparing such gels to set in any desired time. The water glass used showed a ratio of 1  $\text{Na}_2\text{O}$  to 3.66  $\text{SiO}_2$ . The time of set of gels varied with the different acids under similar conditions. Gels containing a very slight excess of hydroxyl ions set in the shortest time, almost immediately if not too dilute. But with increasing excess of hydrogen ion the time of set rapidly increases. With each acid mixed with sodium silicate there is a concentration of hydrogen ion which delays the set to an indefinite time. At still higher concentrations of a given acid the time of set of the gel again becomes measurable, rapidly decreasing to an almost immediate set.

Basic gels are readily prepared by using slightly less acid than is required to neutralize the sodium silicate. Crystalline basic salts may be prepared by diffusion of reacting solutions through such basic gels. The geologist will find reactions in silicic acid gels of either basic or acidic reaction very useful in paralleling crystal formation in nature. One reacting salt may be mixed with the gel material before setting and the other salt solution (osmotically stronger) placed on top of the gel after setting. The slow diffusion resulting aids in formation of good crystals and even of rhythmic bands (Liesegang's rings). This diffusion argues for "brush-heap" structure. For detailed directions my paper<sup>13</sup> on "Formation of Crystals in Gels" may be consulted.

For example, equal volumes of water glass (1.16 density) and 45 *N* phosphoric acid when mixed yield an excellent gel in a very few minutes. Evidently the dehydrating influence of nonionized molecules of the acid mixed with the sodium silicate

<sup>12</sup> *J. Phys. Chem.*, **22**, 510 (1918)

<sup>13</sup> *Ibid.*, **21**, 709 (1917); *J. Franklin Inst.*, **184**, 743 (1917)

is an important factor. A rise in temperature also hastens the set.

Silicic acid gels exhibiting great tendency to contract may be prepared although this is not a general characteristic by any means. Holmes, Kaufman and Nicholas<sup>14</sup> added a water glass of 1.15 density to an equal volume of 6 *N* hydrochloric acid. After pouring this mixture into a heavy milk bottle (pint size) until half filled the bottle was corked and allowed to stand. After a few days the bottle and gel vibrated with a rich musical tone when tapped against wood. A similar mixture poured into a bottle lined with vaseline contracted greatly after setting and squeezed out much liquid (syneresis). It vibrated only slightly on tapping. The gel adheres to glass and on contracting acquires the rigidity due to tension. Since this gel does not adhere to vaseline it is free to contract and pull away from such surfaces, which it does.

The syneresis referred to above is a very common phenomenon with solvated substances. Even gelatinous precipitates squeeze out a water solution and become more compact. The development of "curds and whey" from milk and, perhaps, the staling of bread are examples. When equal volumes of a water glass (1.12 density) and 0.8 *N* citric acid are mixed the resulting gel finally squeezes out much water solution. Equal volumes of a water glass (1.10 density) and *N* acetic acid serve as well.

Patrick and his co-workers have shown that on washing and drying silicic acid gels (and, in fact, many other gels) the loss of water leaves a network of submicroscopic capillaries. This effect is best achieved by "activating" or drying at 150° or even 300°. Holmes and Anderson, in a paper read at the New Haven meeting of the American Chemical Society, April, 1923, showed that precipitation of sodium silicate by addition of ferric chloride yields a gel made up of an intimate mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , both hydrated. On drying, washing and activating this gel it showed excellent ability to adsorb different gases such as benzene, sulfur dioxide, water, gasoline and many others. Seeking to increase the porosity of this gel these authors treated the dried gel with dilute hydrochloric acid which converted the ferric oxide into soluble ferric chloride, easily washed out. A pure white "silica gel" was secured.

<sup>14</sup> *J. Am. Chem. Soc.*, **41**, 1329 (1919)

Its adsorptive power towards a number of gases was much greater than that of the silica gel prepared by Patrick's process. Since that paper was read these workers have prepared a still more active silica gel by removing nickel oxide from an intimate gel mixture of nickel oxide and silicon dioxide. This was done by soaking the green gel in dilute hydrochloric acid and washing out the nickel chloride. While Patrick's gel adsorbed about 33 per cent. of its own weight of benzene from a stream of air saturated with this gas at 30° the gel derived from the nickel oxide material adsorbed 100 per cent. Because of the great industrial importance of adsorption by such activated gels, patents have been sought and obtained on a number of these processes.

#### DISCUSSION ON H. N. HOLMES' PAPER

##### GEL FORMATION

J. ALEXANDER: In all of the very interesting experiments that Dr. Holmes has brought before us here, it seems to me that in some of the cases, and probably in all of them, the nature of the gel would be very materially altered by the degree of concentration. As a consequence things which may happen in concentrated solutions do not necessarily happen in dilute solutions, and *vice versa*. Although under certain circumstances it is possible to get a thread structure, in a great many of our practical gels we do not actually have it.

One of the things which would seem to be influential in the formation of gels is what may be termed water protection. It would seem that it is possible for a substance to "stymie" itself, that is, a certain percentage of the substance reaches the colloidal state, and another part does not; and that part which reaches the colloidal state first interferes with the coagulation of the other portion.

F. C. WHITMORE: I am an organic chemist. I would like to say that most organic chemists have run into this so-called "false gel." I would like to ask whether it is not possible that these silicic acid gels can be explained on the same brush-heap idea?

R. A. GORTNER: Those of you who want something to demonstrate under a microscope and do not want to go to the trouble of making up a gold sol should dissolve about a hundredth

of a gram of dibenzoylcystine in a little alcohol and put in a few drops of water. You get the effect of a lot of small crystal phases. I have been unable to get the halo around these particles, which makes me rather skeptical about the hydration hypothesis. Here we have a substance which sets to a rigid gel, yet we cannot get any evidence whatsoever of hydration in this gel. We can get no evidence of it in the crystal structure whatsoever.

J. ALEXANDER: One thing I would like to bring to the attention of the people here, Dr. Scherrer did some work which enabled us to go even below the limits of the ultramicroscope. By the use of X-ray analysis he found that the particles of colloidal gold are crystalline. Even in the ultramicroscopic bodies he found positive evidence of crystal structure, so that as far as we know, any aggregate of gold, no matter how small it may be gives evidence of being crystalline. The important point is that colloidalilty is quite independent of whether the particles are crystalline or not.

J. H. MATHEWS: As I understand it, Dr. Holmes, you said that when the gel structure is once broken it does not reform.

H. N. HOLMES: That is generally true of the stiffer gels. However, many weaker gels may set again after stirring.

J. H. MATHEWS: We have an interesting case to report. Gold chloride, under certain conditions of concentration that we have never been able to duplicate, will peptize aluminum ethoxide and there results a straw-colored gel. If this is shaken violently, it all goes to pieces and is just as limpid as water. Then if it is let stand for a while, it will come back to its original state, and then upon shaking violently it will again break up and be as limpid as water. This can be repeated *ad infinitum*. We have never been able to duplicate the results, as the concentration limits seem to be very narrow.

An interesting instance of what may be construed to indicate a definite structure in a gel came to my observation a number of years ago. A former student showed me a sheet of hardened gelatin which had broken under strain and instead of a straight break the edges showed a perfectly regular serrated appearance. The individual units of this serrated edge were all of the same proportions, though not all quite the same size and were hook-like in form. These "hooks" were about

three-fourths of an inch long, with sharp points and perfectly sharp edges. A preëxistent structure in the gel seems to me to offer the only plausible explanation of this phenomenon.

S. E. SHEPPARD: I would just like to offer a duplicate of Prof. Mathews' description. I have had a number of instances, either similar to his or bordering on them. One curious case—this case was a photographic emulsion—which showed a sort of convoluted snake-like formation: this had dried away, breaking off in a whole mass of these convolutions. Another one was something like this (illustrating on board); a developed negative was sent back, which I believe had been hardened, and the gelatin had separated from the glass, chipping the glass off, but at the same time taking the shape of a rectangular mass of material, that ran out into points, in the manner described by Dr. Mathews. These things must have something to do with the structure and formation of the finished gel and of the dry gelatin gel. I would like to mention, too, regarding the formation of gels, the preparation of pyroxylin gels. Dissolve pyroxylin in about a 50-50 alcohol-ether mixture, then if you can remove the alcohol from that very slowly, you get a very good gel. If you put this solution in an open bottle, the ether will evaporate more rapidly than will the alcohol and you can get very beautiful gels in that way.

W. G. KELLY: We have tried some experiments with gels of rubber solutions. We get exactly the same results that we have in silicic acid gels. So far as I can see, all the other gels seem to have more or less crystalline structure, but as yet nobody has been able to discover a crystalline structure in rubber. Maybe there is, but we haven't been able to find it.

L. H. REYERSON: An interesting point in the setting of these silicic acid gels is that at high concentrations you get a clear gel, and then as you go down in concentration you get an opaque one, and after that it is perfectly clear again, and those clear gels are better gas adsorbents than the intermediate ones. Those experiments are just the beginning of some work that we are doing in that connection. We are also trying to get the  $p_H$  value. We have run into a good many difficulties, but we expect to overcome them. If we come at it from the acid side, we find the gel will set usually at a  $p_H$  of about 6; going at it from the other side they will set at a  $p_H$  of about 9.

We are just carrying out some experiments to see if we can bring the hydrogen-ion concentration to a narrower limit. There are other interesting factors coming in there that I won't mention at this time.

N. E. GORDON: In connection with the gel formation, in working with alumina gels we have had occasion to make a gel very similar to the type Prof. Mathews spoke about. Perhaps alumina gel has as much variation. It is hard to repeat, to get two gels exactly alike, but we have repeated it twice where that has been the case, but that is all.

J. A. WILSON: Regarding the formation of the structure in gelatin films, it may be of interest to mention an observation I made some years ago. In preparing an ordinary starch solution for use as an indicator, I observed on cooling the formation of needles about three-quarters of an inch long and possibly on an average of about one-sixteenth of an inch in diameter, and quite flexible. I tried for half a day to duplicate it again but was unable to get it. I would be interested in knowing if anyone else has ever observed that. If we get it in gelatin and starch, we might get it in rubber.

## THE FORMATION OF INORGANIC JELLIES

BY HARRY B. WEISER

Although the jelly-like type of precipitate is not so frequently encountered, it is rather surprising how many inorganic substances have been obtained in the form of jellies. Thus almost a century ago Berzelius<sup>1</sup> hydrolyzed  $\text{SiO}_2$  and obtained a colloidal solution of silica which set spontaneously to a firm jelly;<sup>2</sup> Crum<sup>3</sup> made an alumina jelly while testing the action of sulphate on a colloidal alumina; Grimaux obtained a firm transparent jelly while purifying by dialysis a colloidal solution of ferric arsenate peptized by ferric chloride<sup>4</sup> and a colloidal solution of hydrous ferric oxide peptized by alkali in the presence of glycerine;<sup>5</sup> Coloriano<sup>6</sup> observed that a rose colored jelly formed momentarily on adding arsenic acid to a warm solution of manganese carbonate; Reinitzer<sup>7</sup> boiled a chromic salt with sodium acetate and after making the solution alkaline with alkali or ammonia and allowing to stand, a firm jelly precipitated; Förster<sup>8</sup> obtained an instable jelly by the hydrolysis of a solution of copper ammonium acetate; Reynolds<sup>9</sup> added KOH to a solution of mercuric chloride containing acetone and obtained a colloidal solution which set to a jelly on acidifying slightly or on long standing after purification by dialysis; Debray<sup>10</sup> allowed zinc to act on a cold solution of aluminium sulphate and obtained a jelly which he thought was a definite basic sulphate but which Pickering<sup>11</sup> showed was variable in composition; and Rosenheim and Hertzmann<sup>12</sup> heated a colloidal solution of zirconia formed by dialysis of the acetate and obtained a clear transparent jelly. Even from this brief survey

<sup>1</sup> "Lehrbuch der Chemie," 3rd Ed., 2, 122 (1833)

<sup>2</sup> Cf. *Ann. chim. phys.*, [3] 35, 312 (1833)

<sup>3</sup> *J. Chem. Soc.*, 6, 216 (1854)

<sup>4</sup> *Compt. rend.*, 98, 1540 (1884)

<sup>5</sup> *Ibid.*, 98, 1485 (1884)

<sup>6</sup> *Bull. Soc. chim., France*, 45, 711 (1886)

<sup>7</sup> *Monatsh.*, 3, 249 (1883); *Chem. News*, 48, 114 (1883)

<sup>8</sup> *Ber.*, 25, 3416 (1892).

<sup>9</sup> *Proc. Roy. Soc.*, 19, 431 (1871)

<sup>10</sup> *Bull. Soc. chim., France*, 97, 918 (1867)

<sup>11</sup> *Chem. News*, 45, 121, 133, 146 (1882)

one cannot help being impressed not only with the variety of inorganic compounds that can be obtained as jellies but with the apparent diversity in the conditions under which they are formed. It will be noted that all the observations of jelly formation to which I have referred were made accidentally or incidentally in connection with investigations of widely different character. Although no serious attempt has been made to correlate these scattered observations with the end in view of formulating the general conditions of formation of inorganic jellies, they have served as the starting point for more recent investigations on the preparation of jellies. Thus Holmes<sup>13</sup> and his pupils have confirmed and extended Grimaux's observations, showing that several arsenate and phosphate jellies can be formed by dialysis of their colloidal solutions for suitable intervals of time. Bunce and Finch<sup>14</sup> undertook to study the conditions of jelly formation with the end in view of formulating a theory to show why a gelatinous precipitate will form a jelly in certain cases and not in others. They started with chromic oxide that had been obtained in the form of a jelly by Reinitzer. Later Bunce<sup>15</sup> repeated and extended Reynolds work on mercuric oxide jellies and Finch<sup>16</sup> turned his attention to cupric oxide which Förster had found to form jellies under certain conditions. Bunce and Finch studied specifically the effect of different ions on jelly formation but arrived at no general conclusion except that the presence of certain ions seems to be necessary to form jellies. Thus they concluded that acetate or sulphate must be present to get chromic oxide jellies and that a small amount of sulphate is necessary to prepare cupric oxide jellies. Later Nagel<sup>17</sup> showed that there is a limiting concentration of alkali above which a chromic oxide jelly will not form. No theory was advanced to account for the specific effect of ion on jelly formation. Deiss<sup>18</sup> followed up Colorianos' observation and found that clear stable manganese arsenate jellies could be obtained by mixing solutions of  $MnCl_2$  and  $KH_2AsO_4$ . Klemp and

<sup>13</sup> Holmes and Rindfusz, *J. Am. Chem. Soc.*, **38**, 1970 (1916); Holmes and Arnold, *ibid.*, **40**, 1014 (1918); Holmes and Fall, *ibid.*, **41**, 763 (1919)

<sup>14</sup> *J. Phys. Chem.*, **17**, 769 (1913)

<sup>15</sup> *J. Phys. Chem.*, **18**, 269 (1914)

<sup>16</sup> *Ibid.*, **18**, 26 (1914)

<sup>17</sup> *J. Phys. Chem.*, **19**, 331 (1914)

<sup>18</sup> *Kolloid-Z.*, **14**, 139 (1914)



Gyulay<sup>19</sup> prepared jellies of cadmium and zinc arsenate in a similar manner. Pappada<sup>20</sup> believed that colloidal silicic acid was unique since the addition of electrolytes caused a dilute solution to flock while a concentrated solution formed a jelly; but a similar phenomenon was observed by Fernau and Pauli<sup>21</sup> with a colloidal ceric oxide which was precipitated as a jelly by subjecting it to penetrating radium rays or to the action of electrolytes. Pappada expressed the belief that the colloidal particle of silicic acid consists of membranes having a capillary structure which are impermeable to water when charged but which fill up with water forming a jelly when they are discharged by the addition of electrolytes. He did not venture an opinion as to why a dilute colloid flocculates instead of forming a soft jelly. A study of the influence of electrolytes on the velocity of jelling led to the result that with the same concentrations of alkali and alkaline earth chlorides the velocity increases with the atomic weight of the cation and with the magnitude of the charge.

From this résumé it will be noted that the results of recent work on inorganic jellies are specific rather than general just as would be expected in the absence of a working theory. To date the only generalization concerning the formation of jellies is the well known theory of von Weimarn<sup>22</sup> which formulates the effect on the nature of the precipitate of the solubility of a precipitating substance and the initial concentration of the precipitating molecules. From this theory it is deduced that a gelatinous mass will be precipitated when the percentage supersaturation (amount of supersaturation/solubility of coarse crystals) is very great. The accuracy of the deduction has been demonstrated in numerous cases by von Weimarn and others by mixing reacting solutions of high concentrations; and it is apparently true that any salt can be obtained in a gelatinous form if the concentration of the reacting solutions and so the velocity of precipitation is sufficiently high. These are however not the conditions under which jellies are usually obtained. As will be pointed out later the most satisfactory jellies are

<sup>19</sup> *Kolloid-Z.*, **23**, 57 (1918); **23**, 262 (1921)

<sup>20</sup> *Gazz. chim. ital.*, **1903** and **1905**; *Kolloid-Z.*, **9**, 164 (1911); Pappada and Sadowski, *ibid.*, **6**, 292 (1910)

<sup>21</sup> *Kolloid-Z.*, **20**, 20 (1917); *Biochem. Z.*, **70**, 426 (1915)

<sup>22</sup> "Grundzüge der Dispersoidchemie," 1911; "Zur Lehre von den Zuständen

relatively dilute and are prepared by the slow precipitation of dilute colloids under certain conditions or by slow precipitation on mixing dilute solutions where the percentage supersaturation may be relatively small. As a result of his investigations on the preparation of inorganic jellies the author has formulated more specifically the conditions under which jellies would be expected to form and has outlined the effect of various factors such as the presence of different electrolytes, concentration, rate of precipitation, etc., on jelly formation. A summarized account of the work that has been carried out to date in the author's laboratory will be given and the results will be discussed in the light of the general theory.

#### THEORETICAL

It is now quite generally recognized that the formation of a network is an important step in the process of jelly formation. In 1858 Nageli<sup>23</sup> advanced the theory that jellies owe their characteristic properties to a loose network or aggregation of ultramicroscopic or amicroscopic particles. This view was elaborated by Zsigmondy and Bachmann<sup>24</sup> in 1912 and has been supported by recent investigations on silicic acid jellies by Anderson,<sup>25</sup> on starch-water jellies by Meyer<sup>26</sup> and on soap jellies by Bachmann<sup>27</sup> and McBain.<sup>28</sup> The exact nature of the network seems to vary. In certain cases there is a grainy structure and in others, fibrils have been observed, particularly in the soap jellies of Bachmann and McBain. The nature of the fibrils where these occur, likewise seems to vary. In 1914 Stubel<sup>29</sup> pointed out that they resemble linear crystals; in 1913 Flade<sup>30</sup> suggested that jellies in general consist of a texture of (probably) crystalline threads; and in 1916 Howell<sup>31</sup> introduced the term crystalline gel. Bradford<sup>32</sup> considers gel formation as a process of crystallization; but this view is con-

<sup>23</sup> Nageli and Schwendener, "Das Mikroskop," 2 ed., 1877; "Theorie der Gerung," 1879

<sup>24</sup> Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911); *Kolloid-Z.*, **11**, 145 (1912); Bachmann, *Z. anorg. Chem.*, **73**, 125 (1912)

<sup>25</sup> *Zeit. phys. Chem.*, **88**, 191 (1914)

<sup>26</sup> *Kolloid. Chemische Beihefte*, **5**, 1 (1913)

<sup>27</sup> *Kolloid.-Z.*, **11**, 145 (1912)

<sup>28</sup> Laing and McBain, *J. Chem. Soc.*, **117**, 1506 (1920)

<sup>29</sup> *Pflüger's archiv.*, **156**, 361 (1914)

<sup>30</sup> *Z. anorg. Chem.*, **82**, 173 (1913)

<sup>31</sup> *J. of Physiology*, **45**, 26 (1916)

<sup>32</sup> *Biochem. J.*, **12**, 351 (1918)

tradicted by the investigations of Barrett<sup>33</sup> and McBain<sup>34</sup> although both of the latter researchers are strong supporters of a filamentous structure. Harrison<sup>35</sup> agrees that many jellies possess a fibrillar structure but he obtained photographs of gelatine and cellulose jellies that showed the presence of minute particles joined together in a somewhat irregular manner. He believes, however, that Bachmann's and McBain's soap-jellies are crystalline and points out that concentrated aqueous solutions of benzol purpurine and crysophenene set to jellies containing long gelatinous needle crystals, some of them so fine that they can pass almost unbroken through a filter paper with the aid of a vacuum pump. Similarly he states that cholic acid can be obtained in needle shaped gelatinous crystals so fine that they show a remarkable vibration due to the impact of water molecules. If these fibrils are separate and distinct individuals as Harrison believes, then the gel structure may be considered as an aggregate of extremely fine needle-like crystals. In any event it would seem that in order to get a jelly all that is necessary is to precipitate uniformly throughout a solution a very finely divided crystalline or amorphous substance that adsorbs the solvent very strongly. These finely divided particles may form fibrillar threads or they may unite in a more irregular fashion forming trees, radials or something analogous to a string of beads. The resulting network of myriads of hydrous particles constitute the gel structure. The amount of the dispersed phase that must be present to form a firm jelly is determined by the size of the particles and the extent to which they adsorb the solvent. Since finely divided particles that adsorb water strongly are of primary importance in the formation of a jelly the most promising method for obtaining a jelly consists in precipitating a hydrous substance from colloidal solution. Jellies would be expected to form only when the precipitation takes place at a suitable rate in the absence of a medium that exerts an appreciable solvent or peptizing action. The effect of the presence of salts on jelly formation is determined in large measure by the precipitating and stabilizing action of the ions in so far as

<sup>33</sup> *Biochem. J.*, 14, 189 (1920)

<sup>34</sup> *Loc. cit.*

<sup>35</sup> "The Physics and Chemistry of Colloids and Their Bearing on Industrial Ques-

these influence the amount and velocity of precipitation. In general a slow rate of precipitation is to be preferred if there is no tendency of the particles to grow as a result of the solvent action of the electrolyte. In case of such solvent action a granular precipitate is most likely to result. The addition of an electrolyte to the colloidal hydrous substance in such concentration that rapid coagulation takes place usually produces a gelatinous precipitate and not a jelly. The reason is that time is not allowed for uniform mixing of the colloid with coagulant and the slow uniform precipitation that is necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly. From this point of view the formation of jellies by dialysis of a colloidal hydrous substance is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical value necessary for peptization and precipitation results just as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion.

As I have already pointed out von Weimarn<sup>36</sup> prepared jellies of substances like  $\text{BaSO}_4$  which usually precipitate in the form of crystals by mixing very concentrated (3 *N*–7 *N*) solutions of manganese sulphate and barium thiocyanate. This is not the condition under which jellies are usually obtained, and their existence is temporary. By mixing very high concentrations of materials that react to form an insoluble precipitate, a very large number of particles are formed because of the high degree of supersaturation.<sup>37</sup> Each of the myriads of minute particles adsorbs a little water and so encloses the whole amount of liquid thus forming what has been termed a jelly. These so-called jellies break down on standing on account of growth of the particles and the consequent liberation of adsorbed water. I do not believe that precipitates in which the ratio of mols of water to mols of salt is say 20 : 1 or 25 : 1 should be considered as jellies in the same sense as precipitates in which this ratio is two or three hundred times as great. Very finely divided sand or Fuller's earth may be matted

<sup>36</sup> "Zur Lehre von den Zuständen der Materie," 1914, 21

<sup>37</sup> Bancroft, *J. Phys. Chem.*, **24**, 100 (1920)

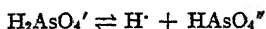
in the bottom of a test-tube and this solid will take up a great deal of water before a supernatant water layer is observed; but I should not call such a preparation a jelly. It seems to me that von Weimarn's barium sulphate jelly may be similar except that the particles are much smaller and so a given amount will take up more water. On the other hand with true jellies where the amount of enclosed water may be relatively enormous, time must be allowed for the formation of a definite structure.

It is impossible therefore to obtain a dilute jelly by von Weimarn's method by mixing solutions of two salts which produce a precipitate immediately even though the precipitate may be highly gelatinous. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solution which is essential for uniform precipitation throughout the solution. One part is precipitated before another is mixed with the precipitant and the homogeneity which is characteristic of a jelly is lost. Moreover the mixing itself will tend to destroy the jelly structure. The results are therefore not unlike those obtained when a colloid capable of forming a jelly by slow precipitation is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a colloidal solution it is necessary to add such an amount of electrolyte that thorough mixing is possible before appreciable coagulation takes place. From these considerations it follows that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate in case the thorough mixing of the solutions could be effected before precipitation began, and in case the precipitation once started proceeded at a suitably slow rate. Such conditions do not obtain as a rule; but they are quite possible theoretically. Thus the precipitation may be the result of a step-wise reaction, one step of which proceeds at a suitable slow rate. It is further possible to have a reaction that proceeds very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would enable one to control the subsequent rate of reaction by a suitable regulation of the temperature.

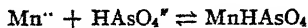
Such a favorable combination of circumstances apparently obtains when a manganese salt and  $\text{KH}_2\text{AsO}_4$  are mixed. The latter salt ionizes thus;



but on account of the solubility of  $\text{Mn}(\text{H}_2\text{AsO}_4)_2$  no Mn ions are removed from solution by interaction with  $\text{H}_2\text{AsO}_4'$ . However the latter ion undergoes secondary ionization to a slight degree as follows:



and insoluble  $\text{MnHASO}_4$  is formed in accord with the following reaction:



Since the precipitation of  $\text{MnHASO}_4$  is accompanied by the formation of an equivalent amount of free H ion in solution an equilibrium is set up which prevents the complete precipitation of the manganese. However, the amount of  $\text{MnHASO}_4$  formed and the rate of formation is apparently influenced to a marked degree by the temperature so that we should be able to realize experimentally the conditions most favorable for the formation of a jelly by direct precipitation from solution.

#### EXPERIMENTAL

##### *Chromic Oxide Jellies*<sup>38</sup>

Attention has been called to Reinitzer's observation that a solution of chromic salt boiled with sodium acetate and rendered alkaline with caustic alkalis or ammonia, sets to a jelly. Bunce and Finch<sup>39</sup> confirmed this observation and showed further that a jelly was formed by adding excess NaOH or KOH to chrome alum and allowing the solution to stand. They were unable to obtain a jelly from chromic sulphate, nitrate or chloride; but Nagel<sup>40</sup> showed that a jelly could be formed with sulphate if the alkali concentration was not too great. From these observations it was logical to conclude that acetate or sulphate ions are necessary for the formation of a chromic oxide jelly.<sup>41</sup> That such is not the case is evident from a series of experiments using chromic chloride instead of sulphate or acetate. The procedure was as follows: A mixing apparatus was prepared consisting essentially of a glass tube 3 cm. in diameter and 10 cm. in length supplied with stoppers. The bottom one contained a glass rod on the end of which was

<sup>38</sup> Cf. *J. Phys. Chem.*, **26**, 402 (1922)

<sup>39</sup> *Ibid.*, **17**, 269 (1913)

<sup>40</sup> *Ibid.*, **19**, 331 (1914)

<sup>41</sup> Bancroft, "Applied Colloid Chemistry," **1921**, 244

sealed a 10 cc. glass cup that was held concentric with the outer tube. In the cup which constitutes the inner compartment of the apparatus was placed 5 cc. of a chromic chloride solution containing 40 g.  $\text{Cr}_2\text{O}_3$  per liter while in the outer compartment was placed a measured amount of standard alkali diluted to 20 or 45 cc. as the case might be. By inverting and shaking the vessel a rapid uniform mixing was obtained. The contents of the mixer were removed to a large test-tube and examined for complete peptization. The nature of the precipitate was observed as given in Table I.

TABLE I  
CHROMIC OXIDE JELLIES FROM NEGATIVE COLLOID

Alkali	Solutions (cc.) mixed			Observation	Nature of precipitate
	Alkali 0.6 N	$\text{CrCl}_3$	Total volume		
NaOH	10.0	5.0	25	Peptization incomplete	Gelatinous
NaOH	11.5	5.0	25	Peptization incomplete	Firm green jelly
NaOH	11.75	5.0	25	Peptization almost complete	Firm green jelly
NaOH	12.0	5.0	25	Peptization complete	Firm green jelly
KOH	10.0	5.0	25	Peptization incomplete	Firm green jelly
KOH	10.75	5.0	25	Peptization almost complete	Firm green jelly
KOH	11.0	5.0	25	Peptization complete	Firm green jelly
$\text{Ba}(\text{OH})_2$	20.0	5.0	25	No peptization	Gelatinous
$\text{Ba}(\text{OH})_2$	24.0	1.0	25	No peptization	Gelatinous
NaOH	13.5	5.0	50	Peptization almost complete	Soft green jelly
NaOH	13.75	5.0	50	Peptization complete	Soft green jelly
KOH	12.0	5.0	50	Peptization almost complete	Soft green jelly
KOH	12.25	5.0	50	Peptization complete	Soft green jelly

Some preliminary experiments showed that the colloidal oxide was readily precipitated by salts; and that the precipitation values could be determined providing a definite method of procedure was followed. The colloid used in the experiments

was prepared by mixing 5 cc. of the chromic chloride solutions used in the earlier experiments with 15.0 cc. of 0.6 N KOH and 30 cc. of water. Since alkali was in considerable excess, the colloid did not start to precipitate for some time unless treated with salts. Ten cubic centimeters of the colloid so prepared was mixed with a definite amount of electrolyte diluted to 10 cc. The precipitation value was taken as that concentration of electrolyte which will just cause complete coagulation in 5 minutes. After determining the approximate precipitation values the exact values were found for each electrolyte with a freshly prepared colloid. The values for a number of salts are given in Table II.

TABLE II  
PRECIPITATION VALUES OF SALTS

Salt	Precipitation value (milliequivalents per liter)	Nature of precipitate
Barium chloride	5.15	Gelatinous
Potassium chloride	500.0	Gelatinous
Sodium chloride	210.0	Gelatinous
Lithium chloride	51.0	Gelatinous
Sodium sulphate	315.0	Gelatinous
Sodium acetate	220.0	Gelatinous

From the results shown in Table II we find that the precipitating power of the cations follows the usual order: barium > lithium > sodium > potassium; and that the stabilizing action of the anions is: sulphate > chloride, acetate.

The experiments recorded in the preceding tables bear out the general conclusions regarding jelly formation. The rapid addition of a slight excess of alkali to a chromic chloride solution produces a negative colloidal oxide that is instable and precipitates slowly forming a jelly (Table I). If this precipitation is hastened by heating or by the addition of a suitable amount of electrolyte, the precipitate forms so rapidly that it is gelatinous but not a jelly (Table II). Since the colloid is negatively charged, it will require the addition of more  $\text{Na}_2\text{SO}_4$ , say, than of  $\text{NaCl}$  to get a gelatinous precipitate on account of the stabilizing action of  $\text{SO}_4$  ion (Table II). Finally, if the hydrous oxide has been peptized by too great a concentration of alkali the precipitate comes down very slowly and is almost granular in character as observed by Nagel.



The results of the experiments on the formation of jellies from negative colloidal hydrous chromic oxide suggested that the positive colloid could be precipitated under conditions favorable for the formation of a jelly. This proved to be unexpectedly easy to do. All that was necessary was to add just enough electrolyte to cause complete coagulation in an hour or two. It was found that if too little electrolyte were used, precipitation was incomplete and the results were unsatisfactory; while if too great an excess were added the precipitation was so rapid that a gelatinous precipitate was formed.

The results given in Table III were obtained with a colloid prepared by peptization of hydrous chromic chloride with  $\text{CrCl}_3$  and dialyzing in the hot until a pure solution was obtained containing 3.65 g.  $\text{Cr}_2\text{O}_3$  per liter. All experiments were carried out in vessels of pyrex glass. The procedure was as follows: In a 25 cc. thick-walled test-tube was placed 10 cc. of colloid; and in a second tube, a suitable amount of electrolyte diluted to 10 cc. The solutions were mixed by pouring from one tube to the other with intermediate shaking; after which the mixture was transferred to one tube that was corked

TABLE III  
CHROMIC OXIDE JELLIES FROM POSITIVE COLLOID

Potassium salt	Precipitation value milliequivalents per liter	Nature of precipitate
Ferricyanide	0.485	Firm transparent jelly
Chromate	0.525	Firm transparent jelly
Dichromate	0.535	Firm transparent jelly
Sulphate	0.550	Firm transparent jelly
Iodate	0.635	Firm transparent jelly
Oxalate	0.660	Firm transparent jelly
Bromate	19.0	Transparent jelly
Chloride	30.0	Transparent jelly
Bromide	33.0	Transparent jelly
Chlorate	33.8	Transparent jelly
Iodide	37.5	Transparent jelly

and set aside for exactly one hour. To determine whether precipitation was complete, the contents of the tube were shaken and centrifuged for 1 minute at 3000 r. p. m. Jellies were obtained in every case in the immediate region of the pre-

cipitation value. In the table are given the precipitation values of a number of salts in milliequivalents per liter. In the last column of the table is given the nature of the precipitate formed by each electrolyte after standing quietly for an hour.

The preceding results show conclusively that jellies will form in the presence of any ion that will effect coagulation of the colloid. It will be noted that the H ion concentration within which jellies will form, can vary considerably. Thus they were obtained from strongly alkaline solution and from a colloid stabilized by H ion.

The following observations give some idea of the nature and stability of the jellies formed by precipitating the positive colloid. Twenty cubic centimeters of a jelly was prepared containing approximately 1 mol  $\text{Cr}_2\text{O}_3$ , 0.002 mol  $\text{K}_2\text{CrO}_4$  and 4700 mols of  $\text{H}_2\text{O}$ . This jelly which is 0.18%  $\text{Cr}_2\text{O}_3$  stood in a test-tube for a week without undergoing noticeable syneresis; and was not broken down by centrifuging for 1 minute at 3000 r. p. m. On shaking, the jelly was destroyed<sup>42</sup> giving a gelatinous precipitate that was thrown down by the centrifuge. A soft jelly was prepared containing but 0.09%  $\text{Cr}_2\text{O}_3$ . Firm jellies of such low concentrations of disperse phase are comparatively rare though Doehle and Rassow<sup>43</sup> obtained jellies of the mercury salt of an organic sulpho acid in concentration of 0.72%; while Förster<sup>44</sup> found that camphorylphenylthiosemicarbazide formed stiff jellies in concentrations of 0.33% and "trembling" jellies in concentrations of 0.25%. Similarly Börjeson in Svedberg's laboratory obtained a jelly when a 0.2 to 0.5% cadmium solution dispersed in alcohol was allowed to stand.

#### STANNIC OXIDE JELLIES<sup>45</sup>

When a colloidal solution of hydrous stannic oxide is evaporated a transparent jelly is obtained; while precipitation with electrolytes is said always to give a gelatinous precipitate and not a jelly.<sup>46</sup> Since hydrous stannic oxide apparently possesses the desired properties, there seems to be no reason why stannic

<sup>42</sup> Cf. Bunce and Finch, *loc. cit.*

<sup>43</sup> *Kolloid-Z.*, **12**, 71 (1913)

<sup>44</sup> Hatschek, *ibid.*, **11**, 158 (1912)

<sup>45</sup> Cf. *J. Phys. Chem.*, **26**, 681 (1922)

<sup>46</sup> Zsigmondy-Spear, "Chemistry of Colloids," **1917**, 155

oxide jellies could not be prepared by precipitation from colloidal solution in the same manner as the chromic oxide jellies. The following experiments confirmed this conclusion. Colloidal stannic oxide was prepared by Zsigmondy's method. 3.5 g. of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 3 liters of water and allowed to stand 3 days. The resulting hydrous oxide was washed by the aid of the centrifuge until it was so free from chlorides that it started to go into colloidal solution. Several of these washed portions were combined, shaken up with water containing a small amount of ammonia and allowed to stand until peptization was complete. The excess of ammonia was removed by boiling which ages the colloidal oxide. The solution used in the subsequent experiments contained 28.3 g.  $\text{SnO}_2$  per liter. Five cubic centimeter portions of colloid were mixed with varying amounts of electrolytes diluted to 5 cc. and the resulting mixture allowed to stand quietly. The colloid was measured with a 10 cc. Mohr pipette graduated in 0.1 cc. The observations after allowing the mixtures to stand 2 days are given in Table IV.

TABLE IV

Formula	Electrolyte		Observations
	Amount added	Concentration (millieq. per l)	
$\text{BaCl}_2$	3.00 cc. <i>N</i> /100	3.00	Clear, transparent jelly
$\text{BaCl}_2$	3.50 cc. <i>N</i> /100	3.50	Clear, transparent jelly; very firm
$\text{BaCl}_2$	3.75 cc. <i>N</i> /100	3.75	Jelly; somewhat cloudy and slightly synerized
$\text{BaCl}_2$	4.25 cc. <i>N</i> /100	4.25	Gelatinous precipitate
$\text{SrCl}_2$	3.50 cc. <i>N</i> /100	3.50	Clear, solution; somewhat viscous
$\text{SrCl}_2$	4.00 cc. <i>N</i> /100	4.00	Clear, transparent jelly
$\text{SrCl}_2$	4.50 cc. <i>N</i> /100	4.50	Clear transparent jelly; very firm
$\text{SrCl}_2$	5.00 cc. <i>N</i> /100	5.00	Cloudy jelly; synerized slightly
$\text{NaCl}$	2.00 cc. <i>N</i> /10	20.00	Clear solution; viscous
$\text{NaCl}$	2.25 cc. <i>N</i> /10	22.50	Soft, cloudy jelly
$\text{NaCl}$	2.50 cc. <i>N</i> /10	25.00	Soft, cloudy jelly
$\text{NaCl}$	2.75 cc. <i>N</i> /10	27.50	Gelatinous precipitate
$\text{HCl}$	1.50 cc. <i>N</i> /50	3.00	Clear solution
$\text{HCl}$	1.75 cc. <i>N</i> /50	3.50	Clear, transparent jelly
$\text{HCl}$	2.00 cc. <i>N</i> /50	4.00	Clear, transparent jelly
$\text{HCl}$	2.25 cc. <i>N</i> /50	4.50	Cloudy jelly; synerized slightly
$\text{HCl}$	2.50 cc. <i>N</i> /50	5.00	Gelatinous precipitate

The results of the experiments given in the preceding table are in accord with the general theory. The jellies formed under most favorable conditions were very firm and stable remaining unbroken after standing several months. They contained 1.4%  $\text{SnO}_2$ .

As was to be expected no jellies were obtained by adding an excess of alkali to a stannic salt and allowing the solution to stand, the reason being that unlike chromic oxide, alkalies have not only a peptizing action on hydrous stannic oxide but a solvent action as well which results in the formation of some stannate even in dilute solution. This solvent action causes the precipitate which comes out spontaneously to consist of large granular particles instead of fine filaments that go to make up the jelly structure.

#### CUPRIC OXIDE JELLIES<sup>47</sup>

As has been stated Förster first prepared cupric oxide jellies by hydrolysis of a solution of cupric ammonium acetate. Finch repeated these observations and found like Förster that the jellies were unstable. A stable jelly was formed by mixing 50 cc. of saturated cupric acetate, 4 drops of concentrated  $\text{H}_2\text{SO}_4$  and 3-4 cc. of diluted ammonia (1 : 1). These observations led to the conclusion that permanent cupric oxide jellies can be formed only by the addition of a suitable amount of ammonia to cupric acetate solution in the presence of a small amount of sulphate ion. No explanation is suggested to account for the facts: first that a limiting concentration of ammonia is necessary; second, that copper acetate is effective but not copper sulphate, chloride or nitrate; and third, that the presence of a small amount of sulphate ion in conjunction with copper acetate is necessary for the formation of a permanent jelly. These facts should find explanation in the light of the general theory.

On adding ammonia directly to 0.75 *N* solutions of cupric acetate, sulphate, chloride and nitrate a bulky precipitate formed immediately. While it enclosed most of the water at the outset it settled quickly leaving a supernatant liquid which proved that it was merely a bulky gelatinous precipitate and not a jelly. Stable uniform jellies are obtained only when

<sup>47</sup> Cf. *J. Phys. Chem.*, **27**, June (1923)

precipitation takes place uniformly throughout the solution at a suitable rate.

The nature of the precipitate formed when copper acetate is precipitated by ammonia in the presence of sulphate was next studied. 25 cc. portions of acetate were mixed with varying amounts of sulphate and treated with ammonia in the mixing apparatus previously referred to. The contents of the mixer were then poured into a large test-tube and allowed to stand. Observations were made each hour until a gelatinous precipitate formed, for the first 6 hours and daily thereafter for two weeks. A part of these observations are recorded in Table V.

TABLE V

Solutions added to 25 cc. 0.75 N Cu (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>		Observations after			
N K <sub>2</sub> SO <sub>4</sub>	$\frac{3}{4}$ N NH <sub>4</sub> OH	4 hours	1 day	7 days	14 days
1	3	Precipitate	.....	.....	.....
2	3	Soft jelly	Precipitate	.....	.....
3	3	Precipitate	.....	.....	.....
4	3	Precipitate	.....	.....	.....
1	4	Good jelly	Soft jelly	Precipitate	.....
2	4	Good jelly	Good jelly	Precipitate	.....
3	4	Good jelly	Fair jelly	Precipitate	.....
4	4	Good jelly	Precipitate	.....	.....
1	5	Good jelly	Good jelly	Fair jelly	Precipitate
2	5	Good jelly	Good jelly	Good jelly	Good jelly
3	5	Good jelly	Good jelly	Fair jelly	Precipitate
4	5	Precipitate	.....	.....	.....
1	6	Fair jelly	Precipitate	.....	.....
2	6	Fair jelly	Precipitate	.....	.....
3	6	Fair jelly	Precipitate	.....	.....
4	6	Precipitate	.....	.....	.....
CuSO <sub>4</sub>					
1	5	Good jelly	Good jelly	Fair jelly	Precipitate
2	5	Good jelly	Good jelly	Good jelly	Fair jelly
3	5	Good jelly	Fair jelly	Precipitate	.....
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>					
1	5	Soft jelly	Fair jelly	Precipitate	.....
2	5	Good jelly	Good jelly	Good jelly	Good jelly
3	5	Good jelly	Good jelly	Good-jelly	Precipitate

Where the term "precipitate" is used, is meant a gelatinous precipitate with considerable supernatant liquid, as distinct

from a jelly. It will be noted that in most cases the jellies are not permanent but break down after a few hours.

The results recorded in Table V show the best conditions for obtaining a firm jelly while closer observations of these experiments indicate the explanation of the results. It was noted at the outset that the addition of less than the equivalent amount of  $\text{NH}_4\text{OH}$  did not produce a precipitate but a perfectly clear solution which starts to precipitate spontaneously after intervals that vary from a few seconds to several minutes depending on the amounts of sulphate and  $\text{NH}_4\text{OH}$  added. We have seen that a comparatively slow precipitation from colloidal solution favors the formation of a firm jelly so that the problem resolved itself into finding the most favorable conditions of precipitation. A firm jelly that remained unbroken for more than 3 months was obtained by adding 5 cc. of 3 N  $\text{NH}_4\text{OH}$  to 25 cc. of 0.75 N  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  containing 2 cc. of  $\text{K}_2\text{SO}_4$ . With too little  $\text{K}_2\text{SO}_4$  a gelatinous precipitate formed at once on adding the equivalent amount of  $\text{NH}_4\text{OH}$ ; the same is true with an excess of  $\text{K}_2\text{SO}_4$ . With a suitable amount of sulphate and too little  $\text{NH}_4\text{OH}$  not enough precipitation takes place to form a firm jelly. This was observed with 3 cc.  $\text{NH}_4\text{OH}$  which is one-half the equivalent of the copper present. With too much  $\text{NH}_4\text{OH}$ , not only does pre-

TABLE VI

Solutions mixed			Observations
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ 0.75 N	$(\text{NH}_4)_2\text{SO}_4$ N	$\text{NH}_4\text{OH}$ 3 N	
25	0.0	1.75	No precipitate
25	0.0	2.00	Very slight precipitate
25	0.2	2.75	No precipitate
25	0.2	3.00	Slight precipitate
25	0.2	3.25	Large precipitate
25	0.4	3.25	No precipitate
25	0.4	3.50	Slight precipitate
25	0.8	4-8	No precipitate. Goes over directly to the blue copper ammonium complex.

cipitation take place too rapidly but a portion of the copper goes to the deep blue copper ammonium complex. This was observed with 7 cc. of  $\text{NH}_4\text{OH}$ , an amount equivalent to the copper. Copper sulphate and ammonium sulphate have the

same effect as potassium sulphate. The action of sulphate was investigated further as follows: 25 cc. of 0.75 *N* copper acetate with or without  $(\text{NH}_4)_2\text{SO}_4$  was placed in the mixing apparatus and a known amount of 3 *N*  $\text{NH}_4\text{OH}$  in the cup. The mixer was shaken and the solutions observed promptly to determine whether or not a precipitate formed at once. By repeated trials the conditions for the formation of a slight permanent precipitate were found with considerable accuracy. The results are given in Table VI.

It will be noted that 2 cc. of 3 *N*  $\text{NH}_4\text{OH}$  must be added rapidly to 25 cc. of 0.75 *N*  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  in order to get a slight permanent precipitate at once. A similar precipitate was obtained on adding but 0.10 cc. of 3 *N*  $\text{NH}_4\text{OH}$  to 25 cc. of 0.75 *N* solutions of  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{CuCl}_2$ . Thus the acetate is the only one of the four salts which gives colloidal hydrous cupric oxide of appreciable concentration on adding  $\text{NH}_4\text{OH}$  to the 0.75 *N* solution. A much higher concentration of the colloid may be obtained by adding to the acetate solution a very small amount of sulphate ion. It is altogether likely that small amounts of multivalent ions other than  $\text{SO}_4^{--}$  would be equally effective but none of the common ions can be employed on account of the insolubility of their copper salts. The colloids obtained in this way of whatever concentration are so instable that spontaneous precipitation takes place on standing. It is this combination of circumstances that enables one to prepare a stable cupric oxide jelly by regulating the conditions so that a suitable concentration of hydrous oxide is allowed to precipitate uniformly at a suitable rate.

#### ALUMINUM OXIDE JELLIES

A colloidal aluminum oxide was prepared by adding an excess of freshly precipitated alumina to hot 8% acetic acid and allowing the mixture to stand for an hour. The colloid so prepared was cloudy and quite viscous. On treating with salts an opaque jelly-like mass was obtained that was not uniform and contained air bubbles.<sup>48</sup> Preliminary investigations showed that clear transparent alumina jellies can be prepared by precipitating colloids formed by a modification of Crum's method<sup>49</sup>

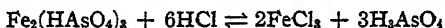
<sup>48</sup> Weiser, *J. Phys. Chem.*, **24**, 525 (1920). Cf. Bently and Rose, *J. Am. Chem. Soc.*, **35**, 1490 (1913).

<sup>49</sup> Weiser, *loc. cit.*

and by Graham's method,<sup>50</sup> but a detailed study has not yet been made.

#### FERRIC ARSENATE JELLIES<sup>51</sup>

Forty years ago Grimaux<sup>52</sup> made the interesting observation that the dialysis of a colloidal solution of ferric arsenate peptized by ferric chloride resulted in the formation of a firm transparent jelly having a reddish-yellow color. More recently Holmes and his pupils<sup>52</sup> have extended the investigations of Grimaux and have found that firm jellies are obtained by the dialysis of colloidal solutions of ferric arsenate peptized by  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{FeCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  but not by  $\text{H}_2\text{SO}_4$  or  $\text{Fe}_2(\text{SO}_4)_3$ . It was pointed out that the formation of a jelly by dialysis of a colloidal solution of ferric arsenate peptized by  $\text{FeCl}_3$  depended on the slow removal of the acid derived from hydrolysis of ferric chloride. It was thought that the equilibrium represented by the following equations was set up:



and that dialysis removed  $\text{HCl}$  permitting the separation of ferric arsenate in the form of a jelly. It seemed that the same result could be obtained by decreasing the  $\text{H}$  ion concentration by the addition of a base; but when this was attempted a lumpy precipitate but not a jelly was obtained. However, jellies were prepared by allowing  $\text{NH}_4\text{OH}$ ,  $\text{Ca}(\text{OH})_2$ , or sodium acetate to diffuse slowly into the colloidal solutions through a membrane of goldbeater's skin.

From the point of view outlined in the theoretical section of this paper the formation of jellies by dialysis of colloidal hydrous substances is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical value necessary for peptization and precipitation results in the same way as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion. With ferric arsenate  $\text{HCl}$  shows both a solvent and peptizing action, but the latter is the only one that is of importance with low con-

<sup>50</sup> *Liebig's Ann*, **121**, 41 (1822).

<sup>51</sup> NOTE: A detailed account of the author's investigations on arsenate jellies will be published in the *J. Phys. Chem.* in the fall of 1923.

<sup>52</sup> *Loc. cit.*



centrations of acid. In the specific case studied by Holmes it seems altogether probable that the reduction of the H ion concentration below a critical value was important largely because H ion happened to be the stabilizing ion. If this is the case then the addition of an electrolyte having a strongly adsorbed cation would neutralize the adsorbed H ion and so would have the same effect as decreasing the actual H ion concentration in solution. Indeed the H ion concentration in the solution might even be increased by the addition of an acid with a multivalent anion that is strongly adsorbed providing the solvent action of this acid is not too great. The accuracy of these conclusions is shown by the subsequent experiments.

Colloidal ferric arsenate prepared as described by Holmes and Arnold by mixing 400 cc. of  $N\text{FeCl}_3$  and 200 cc. of  $N$

TABLE VII  
PRECIPITATION OF COLLOIDAL FERRIC ARSENATE BY ELECTROLYTES

Electrolyte added to 5 cc. colloid	Final volume	Time	Nature of precipitate
5 cc. $N/100\text{ H}_2\text{C}_2\text{O}_4$	10	10 da.	No precipitate
6 cc. $N/100$ "	11	10 da.	Partly precipitated, gelatinous
0 2 cc. $N/10$ "	5.2	7 da.	Perfectly clear jelly
0 3 cc. $N/10$ "	5.3	4 da.	Perfectly clear firm jelly
0 5 cc. $N/10$ "	5.5	1 da.	Firm opalescent jelly
0 6 cc. $N/10$ "	5.6	1 hr.	Firm opaque jelly
4 cc. $N/100\text{ H}_2\text{SO}_4$	9	1 da.	Perfectly clear jelly
6 cc. $N/100$ "	11	1 da.	Firm slightly opalescent jelly
8 cc. $N/100$ "	13	1 da.	Firm opalescent jelly
0 2 cc. $N/10$ "	5.2	4 da.	Perfectly clear jelly
0 4 cc. $N/10$ "	5.4	3 da.	Firm jelly slightly opalescent
0 8 cc. $N/10$ "	5.8	1 hr.	Firm opaque jelly
1.5 cc. $N/10$ "	6.5	2 min.	Gelatinous precipitate
2 cc. $N/100\text{ NH}_4\text{OH}$	7.0	3 da.	Perfectly clear weak jelly
3 cc. $N/100$ "	8.0	1 da.	Firm opalescent jelly
5 cc. $N/100$ "	10.0	1 hr.	Firm opaque jelly
0.1 cc. $N/10$ "	5.1	3 da.	Perfectly clear weak jelly
0.2 cc. $N/10$ "	5.2	1 da.	Perfectly clear firm jelly
0.5 cc. $N/10$ "	5.5	1 min.	Gelatinous precipitate
1 cc. $N/100\text{ Na}_2\text{SO}_4$	6	5 da.	Perfectly clear soft jelly
1.5 cc. $N/100$ "	6.5	3 da.	Perfectly clear firm jelly
2 cc. $N/100$ "	7.0	1 da.	Firm slightly opalescent jelly
6 cc. $N/100$ "	11.0	1 hr.	Opaque jelly

$\text{Na}_2\text{HAsO}_4$  was dialysed for 6 days using the Needle dialyzer. A clear reddish-yellow colloidal solution was obtained which

was quite sensitive to the action of electrolytes. To 5 cc. portions of this colloid were added the amounts of electrolyte shown in the third column of Table VII; and observations were made after allowing the mixture to stand quietly for the period of time noted in the third column. The experiments recorded are taken from a larger series of similar observations.

The preceding results merely emphasize the importance of neutralizing the adsorbed stabilizing hydrogen ion since suitable acids, bases and salts are equally effective in the precipitation of a jelly from colloidal solutions. It will be noted that if too little electrolyte is added no jelly or an imperfect or soft jelly results while if too much electrolyte is used a gelatinous precipitate is obtained. All stages in the process from the formation of weak clear jellies through firm clear jellies and firm opalescent jellies to gelatinous precipitates can be realized by suitable variation in the amounts of the several electrolytes.

Results similar to the above were obtained with colloidal aluminum arsenate.

#### MANGANESE ARSENATE JELLIES

I have pointed out that when dilute solutions of a manganese salt and potassium dihydrogen arsenate are brought together in the cold that the precipitation of  $\text{MnHAsO}_4$  is delayed until a thorough mixture is obtained. Both the rate of formation and the yield of precipitate is increased by raising the temperature. Since the arsenate tends to form a highly hydrous precipitate it should be readily possible to precipitate it as a jelly by mixing the reacting substances in the cold and then warming the mixture or allowing it to stand quietly for some time. This is well illustrated by the experiments recorded in Table VIII. The procedure was as follows: Solutions of  $N$   $\text{MnCl}_2$  and  $\text{KH}_2\text{AsO}_4$  were prepared from freshly boiled water. This precaution was necessary as we found in order to prevent the formation of air bubbles in the jelly. The solutions were cooled to  $0^\circ$  and suitable amounts of each were placed in 60 cc. test-tubes in the ratio shown in the table. The solutions were diluted with cold water either to the final volume shown in column 3 of Table VIII or to an aliquot part thereof. The water was distributed between the two test-tubes so that the volume in each was the same. The mouths of the tubes were

then connected with a piece of large thin rubber tubing used in connection with Gooch filter funnels. Rapid mixing was accomplished by inverting one of the tubes quickly and then promptly throwing the entire contents back into the empty tube. The mixture was set aside for 15–20 minutes and if jelling had not begun the tube was warmed by dipping carefully into boiling water until precipitation started after which it was allowed to stand quietly. In the experiments using  $\text{KH}_2\text{AsO}_4$  it was possible in every case to get complete mixing before precipitation started and excellent clear jellies were obtained. With the secondary and tertiary salts instantaneous formation of a gelatinous precipitate or a cloudy heterogeneous jelly was produced. The results are shown in Table VIII.

TABLE VIII  
PRECIPITATION OF MANGANESE ARSENATE

Electrolytes mixed		Final volume	Nature of precipitate
$\text{MnCl}_2$	$\text{KH}_2\text{AsO}_4$		
10	10	20	Firm jelly almost clear
10	20	30	Firm jelly almost clear
10	20	50	Firm jelly perfectly transparent
10	20	100	Firm jelly perfectly transparent
10	20	200	Soft jelly perfectly transparent
10	20	300	No jelly
..	$\text{Na}_2\text{HAsO}_4$	...	
10	10	...	Cloudy jelly not uniform
10	10	50	Cloudy gelatinous precipitate

The manganese arsenate jellies are unusually clear and perfect and are very stable showing little tendency to cloud up and crystallize after standing a month and they undergo little or no contraction or syneresis on standing.

On heating the jelly crystals of  $\text{MnHAsO}_4$  were formed. Deiss found that about half the theoretical amount of salt was precipitated on mixing solutions of  $\text{MnCl}_2$  and  $\text{KH}_2\text{AsO}_4$  in the approximate ratio given in Table VIII and heating the mixture for 8 hours on the water-bath. The amount of  $\text{MnHAsO}_4$  formed under the conditions of our experiments was doubtless much less but assuming that half the theoretical amount was precipitated it follows that a very firm jelly results with 0.5% and a soft jelly with but 0.25%  $\text{MnHAsO}_4$ .

Good jellies are not obtained by mixing  $\text{MnCl}_2$  and  $\text{Na}_2\text{HAsO}_4$  since the precipitation is instantaneous not allowing time for mixing and the formation of the jelly structure.

## ZINC ARSENATE JELLIES

Zinc arsenate jellies result on mixing a zinc salt with  $\text{KH}_2\text{AsO}_4$  or  $\text{Na}_2\text{HAsO}_4$  under suitable conditions. The jellies formed with  $\text{Na}_2\text{HAsO}_4$  were cloudy and not uniform because of too rapid precipitation. The precipitation was more rapid on adding  $\text{KH}_2\text{AsO}_4$  to a solution of a zinc salt than to a manganese salt. Good jellies were therefore obtained only at fairly high dilutions which slowed down the precipitation and

TABLE IX  
PRECIPITATION OF ZINC ARSENATE

Solutions mixed		Final volume	Nature of precipitate
$\text{ZnSO}_4$	$\text{K}_2\text{HAsO}_4$		
10	10	20	Gelatinous precipitate formed at once enclosing most of the water. Cloudy
10	20	30	Cloudy gelatinous precipitate formed at once enclosing all the water
10	10*	20	No precipitate until after warming. Firm clear jelly
10	20*	50	Gelatinous precipitate formed at once but mixture set to a fairly clear jelly that was not uniform and contained air bubbles
10	20*	50	Excellent clear jelly
10	10	40	Precipitation delayed slightly. Firm jelly slightly opalescent
10	10	60	Perfectly clear transparent jelly
10	20	100	No immediate precipitate. Perfectly clear jelly on warming
10	$\text{Na}_2\text{HAsO}_4$		
10	10	50	Immediate precipitation, cloudy, jelly not uniform

\* 0.1 cc.  $N \text{ H}_2\text{SO}_4$  added before mixing.

allowed time for mixing. It seemed likely that the same result could be accomplished with concentrated solutions by increasing the H ion concentration slightly. This was true as shown by the observations recorded in Table IX.

The results on the formation of zinc arsenate jellies emphasize the importance of preventing precipitation until mixing of the solutions is complete. To obtain good jellies it is necessary to control the condition of precipitation more carefully than with manganese arsenate. Moreover the jellies are less stable and even the dilute ones become cloudy in a few days owing to the formation of crystals. This tendency is much more marked in the case of cadmium arsenate which was obtained only temporarily as a jelly. Copper arsenate could not be precipitated as a jelly; but quite stable cobalt arsenate and ferrous arsenate jellies were prepared.

#### SUMMARY

(1) Hydrous jellies are formed if a suitable amount of a substance that adsorbs water strongly is gotten into colloidal solution and caused to precipitate in the absence of a medium that exerts an appreciable solvent or peptizing action. The effect of the presence of salts on the formation of jellies is determined in large measure by the precipitating and stabilizing action of the ions in so far as these influence the rate of precipitation. In general a slow rate of precipitation is to be preferred in case there is no tendency of the particles to grow as a result of the solvent action of the electrolyte. In case of such solvent action a gelatinous or granular precipitate is most likely to result. The addition of electrolytes to the colloidal hydrous colloid in such concentration that rapid coagulation takes place usually produces a gelatinous precipitate and not a jelly. The reason is that time is not allowed for uniform mixing of the colloid with coagulant and the slow uniform precipitation that is necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly.

(2) The formation of jellies by the dialysis of hydrous colloids is due to the removal of the stabilizing ion slowly and uniformly below the critical value necessary for peptization. Under these conditions precipitation results just as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion.

(3) Uniform dilute jellies are not formed by mixing solutions of two salts which produce a precipitate immediately even though the precipitate may be highly gelatinous. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions which is essential for uniform precipitation. One part is precipitated before another is brought in contact with the precipitant and the homogeneity which is characteristic of a jelly is lost. The results are therefore not unlike those obtained when a colloid capable of forming a jelly by slow precipitation is coagulated too rapidly by the addition of excess electrolyte.

(4) A hydrous substance may be precipitated in the form of a jelly by metathesis in case the thorough mixing of the solutions can be effected before precipitation begins and in case the precipitation once started proceeds at a suitably slow rate. Such conditions do not obtain as a rule but they are quite possible theoretically and have been realized experimentally.

(5) Results on the formation of inorganic jellies that are in accord with the general propositions outlined above have been obtained with chromic oxide, stannic oxide, aluminum oxide, cupric oxide; and with the arsenates of ferrous and ferric iron, aluminum, zinc, cadmium, cobalt and manganese.

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[CONTRIBUTION FROM THE KAISER WILHELM INSTITUTION FOR  
PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, BERLIN, AND THE  
COLLOID LABORATORY OF THE UNIVERSITY OF WISCONSIN]

## THE FORMATION OF MANGANESE ARSENATE JELLIES

BY ELMER O. KRAEMER

It is often difficult to prepare certain crystalline substances, insoluble in water, by double decomposition reactions between two suitable solutions. That is, instead of obtaining a definitely crystalline precipitate of the desired insoluble material, one may find that the entire reacting system sets to form a more or less clear elastic jelly. For instance, it is possible to prepare jellies of the phosphates and arsenates of some of the metals by mixing solutions of a soluble salt of the metal and an alkali phosphate or arsenate. However, our present knowledge concerning the conditions under which a precipitate (in the ordinary sense) or a jelly will form is rather meager. Since, in such a situation, every new fact is valuable, I should be pleased to make a preliminary report of some observations which I have made on the formation of precipitates and jellies of manganese arsenate.

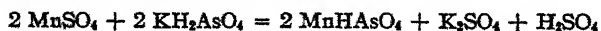
Of course there is no sharp line of demarcation between a precipitate and a jelly. Starting with a definitely crystalline precipitate, one may form a perfectly continuous series of solvated gelatinous precipitates, weak mushy jellies and clear, firm and elastic jellies. However, it was found that under proper conditions a rather clear elastic jelly of manganese arsenate could be prepared which would "set," *i. e.*, become solid, in 10-20 seconds. By a suitable change in conditions, the time of set could be increased with the formation of clearer, more transparent jellies. Or on the other hand, the time of set could be decreased with the formation of turbid mushy jellies containing more or less precipitate. Jellies and precipitates were therefore distinguished on the basis of "time of setting."

The "time of setting" was determined in the following way. A measured volume of a solution of manganese sulphate, for instance, was added quickly to a measured quantity of an alkali arsenate solution in a beaker. The contents of the beaker

were mixed quickly by whirling briskly. The motion of the small fibers or air bubbles was then observed. The motion became slower and slower until it stopped with a distinct jerk, showing the rather sudden appearance of elastic properties in the jelly. The time between the mixing of the solutions and this setting of the jelly was measured with a stop-watch (usually between 10 and 20 seconds). After a little practice in standardizing the technique, it was found possible to duplicate results to 4-5%—which is as good as can be expected. Using this method, the influence of various factors on jelly formation was studied.

#### EFFECT OF CONCENTRATION OF REACTING MATERIALS

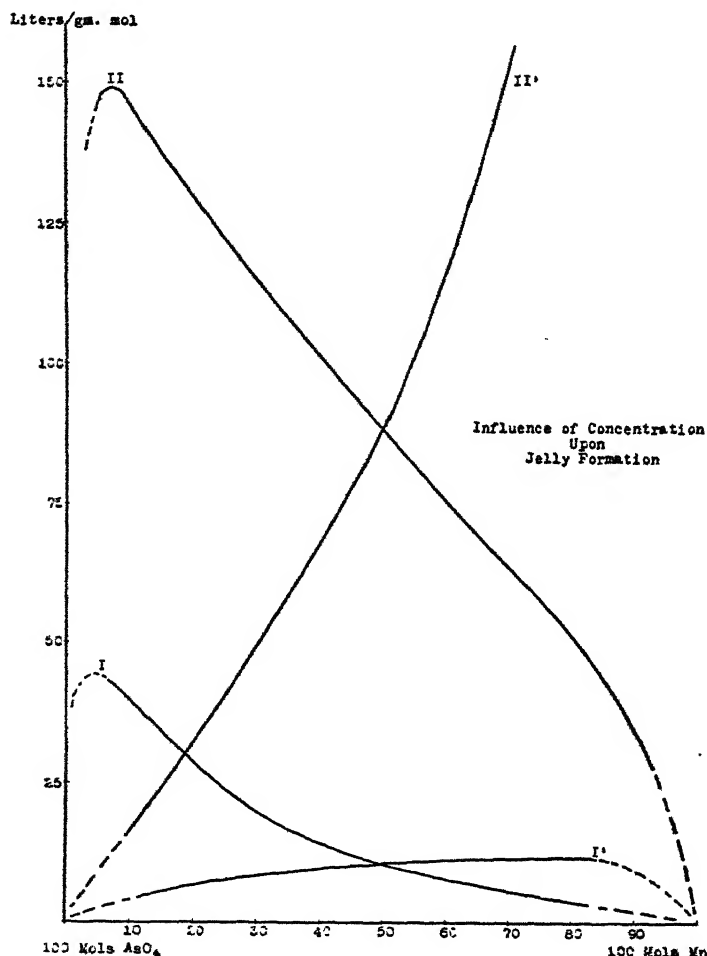
If concentrated solutions of manganese sulphate and potassium dihydrogen arsenate are mixed, a heavy gelatinous precipitate is in general obtained. By proper dilution, however, clear transparent jellies may be formed. With varying proportions of manganese sulphate and potassium arsenate, the concentrations were determined which were necessary for the formation of jellies in a constant time, *e. g.*, 10 seconds. We may show the results graphically by plotting on the X-axis the composition of the solute, and on the Y-axis the number of liters containing one mol of manganese after mixing has taken place. (See Curve I.) It may be seen that as the excess of potassium arsenate was increased, it was necessary to dilute the system more and more to prevent the formation of a precipitate until finally a maximum was reached when the ratio of potassium arsenate to manganese sulphate had reached a value of 94/6 mols. On the other hand, with excess of manganese salt, the concentration of the reacting materials had to be increased in order to obtain jellies setting in 10 seconds. If the dilutions with respect to potassium arsenate be plotted, we obtain Curve I'. This latter curve is fixed and determined by the Curve I, *i. e.*, the ratio between the corresponding ordinates of the two curves for a given value of  $x$  is equal to  $x$ . Assuming that the dispersed phase of the colloidal system is manganese hydrogen arsenate, we may indicate the chemical reaction by the following equation:



The left half of Curve I together with the right half of Curve



I' show the relationship between the concentration of manganese arsenate and the ratio of the reacting materials *under the particular conditions under which these jellies were formed.*



It is meaningless to attempt to show graphically the relation between jelly or precipitate formation and the total quantities of substances in the system after mixing because these factors alone do not determine the character of the dispersed phase. The rapid drop in the curve with increasing manganese is due

to the fact that the concentration of the sulphuric acid formed in the reaction increases and favors the formation of a jelly.

With manganese nitrate instead of manganese sulphate, an entirely similar curve was obtained. In this case, the nitric acid formed in the reaction is responsible for the drop in the curve as the manganese arsenate increases.

With manganese acetate and potassium dihydrogen arsenate, a quite different curve was obtained. (See Curve II.) Due to the weakness of the acetic acid formed and also due to the fact that the acetate ion appears to favor precipitate formation, the dilutions must be much greater to make possible jelly formation. It is worth noticing that at such dilutions manganese sulphate or manganese nitrate form neither jellies nor precipitates.

#### CATION EFFECT

It was found that the addition of certain salts hindered precipitate formation and favored jelly formation. The influence of the cation was measured by determining the quantities of sodium, potassium, ammonium and lithium sulphates necessary to prevent precipitate formation and make possible jelly formation in a given system of manganese sulphate and potassium arsenate. The effectiveness was in this order:

H: Li: NH<sub>4</sub>: Na: K: : 55.5: 1.55: 1.48: 1.16: 1

The effect is therefore rather small and about uniform for the alkali cations.

#### ANION EFFECT

In an analogous fashion the effect of the anion was determined by using various potassium salts. The concentrations necessary to change a given precipitate-forming system to a jelly-forming system (setting in 10 seconds) are given below.

	Molarity	
C <sub>2</sub> O <sub>4</sub> .....	0.005	} Favor jelly formation
SO <sub>4</sub> .....	0.033	
CNS.....	0.092	
Cl.....	0.333	
NO <sub>3</sub> , ClO <sub>3</sub> .....	0.500	
	Relative molarity	
Tartrate.....	1	} Favor precipitate formation
Acetate.....	5	

The two groups given above are not comparable.

The same series and relative values were found using both manganese sulphate and manganese nitrate solutions as reagents.

#### INFLUENCE OF ACIDS

Acids are very effective in preventing precipitate formation and favoring jelly formation. The relative effectiveness of the various acids is inversely proportional to the concentrations necessary for preventing precipitate formation. These relative concentrations are given below.

	Normality		Molarity
Oxalic.....	0.00612	Citric.. . . .	0.00300
Dichloroacetic.....	0.00730	Oxalic.....	0.00306
HCl-HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> -H(H <sub>2</sub> AsO <sub>4</sub> )...	0.00750	H <sub>2</sub> SO <sub>4</sub> .....	0.00375
HCNS.....	0.00760	Tartaric.....	0.00425
Monochloroacetic....	0.00770	Dichloroacetic..	0.00730
Tartaric....	0.00850	H <sub>2</sub> AsO <sub>4</sub> ....	0.00735
Lactic . . . . .	0.00900	HCl-HNO <sub>3</sub> ....	0.00750
Citric.....	0.00900	HCNS.....	0.00760
H <sub>2</sub> (HAsO <sub>4</sub> ).....	0.01470	Monochloroacetic.	0.00770
H <sub>2</sub> AsO <sub>4</sub> . . . . .	0.02200	Lactic.....	0.00900
Acetic... . . . .	0.02800	Acetic... . . . .	0.02800

It is to be seen that in the case of the strong acids the influence of the H ion predominates, but that in the case of weaker organic acids the influence of the anion asserts itself.

#### INFLUENCE OF NON-ELECTROLYTES

Urea favors precipitate formation in accordance with its basic character.

Alcohol also prevents jelly formation.

Dextrose has only a slight effect at the most.

#### INFLUENCE OF TEMPERATURE

As might be expected, temperature is an important factor in determining whether under given conditions, a jelly or a precipitate will form. In the case of manganese arsenate jellies, lowering of the temperature favors a jelly-formation, and on the basis of the speed of setting, the temperature-coefficient is about 500% for a 10° change in temperature.

#### GENERAL FEATURES

The manganese arsenate jellies show a number of interesting

features which are rather difficult to explain. The jellies with excess manganese salt, upon aging, show rather strong syneresis. After a time small spherical groups of rose-colored crystals appear scattered through the jelly. With further aging, these crystals grow and the jelly becomes weaker and weaker until the crystals rest on the bottom beneath the supernatant liquid.

The supernatant liquid however is not free from colloidal material. Increase in temperature or the addition of potassium acetate produces either a precipitate or jelly.

In the case of the jellies with an excess of arsenate present, practically no syneresis takes place, nor do crystals appear. I have here a jelly now 7 months old, which looks just as it did the day after its preparation. The liquid pressed from the jellies, even after aging several months, also contains colloidal material.

With these facts before us, it is not possible to state definitely just how each variable exerts its influence upon jelly or precipitate formation. We may well suppose, however, that the formation of a jelly or precipitate takes place in a number of steps. In the case, of a double decomposition such as we have in this case, the first step after the chemical reaction is probably the separation of the nuclei of the precipitating material. These nuclei are extremely small, being almost of molecular size. The velocity of their formation as well as their number are influenced not only by the specific supersaturation according to von Weimarn, but also by the presence of foreign substances as the solvent, reacting substances or products of reaction. These nuclei grow into the region of colloidal particles where surface effects become quite pronounced. The velocity of growth of the nuclei may well be influenced by adsorption of foreign materials present. Due to the presence of electrolytes these particles may first take on an electrical charge and then lose it with the result that agglomeration takes place. The velocity of this agglomeration is probably determined by the materials present in the system. The character of the agglomerated particles is determined by the specific ions adsorbed on the surface of the particles, particularly by the tendency of the adsorbed ions to sheath the particles in a protecting layer of water. The complete and rapid discharge of the particles may lead to a denser type of

agglomerated particle, *i. e.*, one which settles out as a precipitate. To form jellies, the particles are perhaps smaller and are rather loosely knit together to form a loose sponge-like structure which holds within itself the dispersion medium. But all this must remain supposition until means are found for actually separating the factors involved and determining just how the foreign materials influence each of these various stages in the formation of a jelly or precipitate, particular emphasis being placed upon the changes in the *velocities* of the separate steps. Until we can do this, we shall not be able to specify definitely and quantitatively the conditions for jelly or precipitate formation.

JOINT DISCUSSION ON H. B. WEISER'S PAPER  
THE FORMATION OF INORGANIC JELLIES  
AND E. O. KRAEMER'S PAPER  
THE FORMATION OF MANGANESE  
ARSENATE JELLIES

N. E. GORDON: This is certainly an important work, and very interesting indeed, and I was especially pleased by the manner in which the last man supplementarily summed up the situation. I don't like to see new theories advanced until we see that the old ones will not explain things. He is right when he says that so far as we have gone the old theory will explain it, as far as we can understand these matters. As far as his theory is concerned, we know that it depends upon the original formation of those original nuclei and the rate of growth. Now these various things that have been added, it seems to me, affect those factors, and as far as I have seen from our work, I can't see that we can go much farther, but I do think that it is very important to have the scientific access. I do not see, if there is any other theory, what the other theory is. I am asking for information on that point, *i. e.*, where the new theory that has been advanced adds anything to the old theory.

H. B. WEISER: I do not think, inasmuch as I have discussed von Weimarn's theory in a general way that I have disregarded it to the extent of substituting another theory for it. Von Weimarn formulates the conditions for forming jellies and prepares them by the interaction of concentrated solutions

where low solubility and a high percentage supersaturation obtain and so where very rapid precipitation takes place. This is certainly not the usual method for obtaining typical inorganic jellies and so the von Weimarn theory is not without its limitations. Thus it does not tell us why a slow rate of precipitation from a very dilute colloidal solution will form a jelly in certain cases while rapid coagulation gives a gelatinous precipitate; nor does it cover the cases I have noted where dilute jellies are formed by slow precipitation from solutions where the percentage supersaturation is very low and where there is an appreciable solvent action which von Weimarn found destructive to jelly formation. Accordingly, I have outlined the general conditions that favor the formation of the usual dilute inorganic jellies and have discussed these factors in a decidedly more specific manner than von Weimarn has ever done or than could be deduced from von Weimarn's formulation. I am not expecting credit for attempting to go further than this.

I was interested in this last paper to note that it seems altogether probable that the general considerations which I have outlined may be of such value that the data, if we can sit down and study them out, will fall definitely in line. There is one point, however, that it seems to me should be mentioned in this connection, namely, that the distinction between the formation of jellies and the formation of gelatinous precipitates is rather vague. I am disposed to feel that the time element is such an important thing that many of the substances which have been said to form gelatinous precipitates would really form jellies if they were allowed to stand longer. The distinction in such cases is rather a distinction between the amounts of material that have come out in a given unit of time. For that reason I am not exactly certain what these results will tell us.

J. ALEXANDER: I have had occasion to review a good deal of the literature in that direction, and I wonder whether the whole situation here could not be to some extent clarified by considering two general tendencies in the formation of jellies, the one tendency would be for the formation of colloidal particles and the other tendency would be the aggregation of those particles into groups. By the way, may I ask, whether you have ever tried the effect of protective colloids?

H. B. WEISER: No. We purposely avoided the use of protective colloids.

J. ALEXANDER: I think it would be very interesting for you to find out the effect of protective colloids. Certain factors, too, tend to make these individual particles grow and other factors tend to aggregate them, and the net result is going to depend upon the summation of these two effects. For example, if you take a colloidal metal and coagulate it, as a rule the result will be that the particles that form do not hold water, they begin to shed water right along. The water in them is squeezed out. Therefore the state of water adsorption is highly important. I took some gum, which swells up in cold water, and by heating it managed to drive off considerable water, and then by grinding it up and soaking it up in water against gum in the same condition I found that in the case of the gum that would swell it was all right, but in the other case we got a gelatinous precipitate. So the state of swelling of these particles is exceedingly important, especially when we recall that one of Zsigmondy's pupils, regarding the behavior of stannic oxide gel, pointed out that the individual colloidal particles must be about seven-eighths water, only about one-eighth being really  $\text{SnO}_2$ . So then I imagine that in all these cases we have various coagulating tendencies on the part of the substance liberated, so that we have to consider the effect first on the growth of the particle—the speed of a particle, the specific hydration capacity of the particle, and then the aggregation tendencies of the various substances appearing, and in all this matter, time is a very important factor. Here, too, as in all matters of this kind, we can't get away from specific effects. The reason seems to be that atoms are definitely and differently constituted, and act differently.

E. O. KRAEMER: With respect to the action of protective colloids, I made a few experiments using gelatin, but I did not find any effectiveness in the gelatin as a protective agent. Then I decided that this perhaps is due to the fact that the velocities of the changes taking place during the formation of the jellies are so rapid that the protective action does not have time to take place. That is, we know that the protective action in general is not immediately effective after the addition of gelatin, but that a certain time is necessary for the ad-

sorption of the protective colloid on the colloid particles to be "protected." In these cases the changes leading to gel-formation are too rapid to allow that protective action to show itself.

J. ALEXANDER: Have you slowed down the action?

E. O. KRAEMER: I have used only gelatin in attempting to slow down the rate of gel-formation.

J. ALEXANDER: Will any of these things coagulate the gelatin or practically drive it out of the solution, or kill it?

E. O. KRAEMER: I cannot say. Regarding Dr. Weiser's remarks, I appreciate and emphasized in my paper the fact that the "time of setting of a jelly is a somewhat indefinite quantity." However, it was found that in the case of the manganese arsenate systems, a rapid reaction leads to gelatinous precipitates and supernatant liquid, while a slower reaction leads to formation of firm, elastic jellies. Furthermore, a parallelism exists between the rate of formation of these jellies and their appearance and properties such as turbidity, elasticity, firmness, etc. We possess no means for distinguishing sharply between gelatinous precipitates and jellies. Practically all the available data on jelly formation including that of Dr. Weiser's are based on distinctions between jellies and precipitates which are even less definite than that furnished by "time of setting." Such data tell us practically nothing in a *quantitative* way concerning the influence of various factors on jelly formation. The quantitative data obtained by "time of setting" studies therefore justifies my method.

H. B. WEISER: It is true that the time of setting may have been the only thing available in a reasonable length of time, but it is perfectly possible to make these jellies in such a way that one will set and another will not set if you will allow time enough. One will set in a little while and another will not set in an indefinite time. While that would prolong the investigation a great deal, it would give an indication of whether you get a jelly in one case and whether you fail to get a jelly in another. The way it is, you would get a jelly in nearly every case, if sufficient time were allowed. I was just suggesting that if it had been possible for you to have stretched the thing out for a longer period of time or to have worked with more dilute solutions, different results might have been obtained.



I do not know that this would affect the data, but the analysis of these results in the light of the general conditions which I have outlined is made rather difficult because I do not know exactly what we have here.

E. O. KRAEMER: In these experiments, I was particularly interested in the conditions necessary for the formation of jellies and of "precipitates" shortly after the chemical reaction had taken place, independently of whether a crystalline precipitate would develop after long standing or not. In my observations with more dilute solutions I never observed *any* precipitate formation, gelatinous or crystalline. Examinations of my curves showing the influence of dilution upon jelly-formation will show that the boundary region which I studied lies between the region of "gelatinous precipitate" formation and "jelly formation." My method of study is possible only in this region. And study of more dilute systems as Dr. Weiser suggests would give no information concerning that boundary region between gelatinous precipitates and jellies which I studied.

H. B. WEISER: Although Mr. Kraemer has apparently found that satisfactory data are furnished by "time of setting" even when such concentrations of solutions were employed that the time interval lies within ten seconds, I think he is quite mistaken in his belief that the distinction between gelatinous precipitates and jellies is always so indefinite that data based on this distinction tell us practically nothing in a quantitative way concerning the influence of various factors on jelly formation. I need mention but one instance. In my investigations on the effect of salts on jelly formation in the immediate region of their precipitation values for colloids, I have found time and time again that an extremely small difference in concentration determined whether a typical gelatinous precipitate with supernatant liquid would form or whether a typical jelly that remained unbroken for weeks would result. The quantitative accuracy of such data is probably of a different order than those furnished by a ten second time of setting.

In my original paper on arsenate jellies, now in press, I pointed out that the hydrogen-ion concentration is such an important factor in determining the amount and rate of pre-

cipitation that only zinc salts of the stronger acids could be used to form jellies by interaction with  $\text{KH}_2\text{AsO}_4$ . This was verified. With zinc acetate, gelatinous precipitates were formed at all temperatures and dilutions. The same seems to apply to the manganese arsenate jellies as well. At the time it seemed impracticable to attempt to make an extended study of the effect of various anions. The same applies to the manganese salts. Where such slight solubility obtains, it is difficult if not impossible to determine to what extent the added anion is removed before the hydrous arsenate starts to form. The effective concentration of the anion in such cases is an indefinite quantity. Moreover since the hydrogen-ion concentration is such a very important factor in the process, it is difficult indeed to evaluate the specific effect of the anion alone.

F. DANIELS: I would like to ask for more information about the distinction between the "false gel" and the "real gel." Is this a sharp distinction or is it merely a matter of time? Will the real gel become crystalline or is it in a stable condition? I understood Dr. Holmes to say that possibly syneresis could be explained on the basis of crystallization in a real gel. The point is not important now but eventually we will return to the "RT's" and the "dT's", and when we apply thermodynamics it will be important to know whether we have a real equilibrium or a false equilibrium.

H. N. HOLMES: In reply, syneresis may well follow from a development of larger crystals from a very fine network structure. On the other hand, take the silicic acid gels, we must, as you suggest, name a basis for them. The false gels I used Tuesday morning, furnish an extreme case and the divisions between these things are then quite arbitrary. I gave you the caffeine "false gel" for example. The water was held in a very loose way, but still it was held. That was one end of the line, and certainly we had a false gel there, but when we go to the other extreme where I believe the solvent is held rather firmly, I would call that a true gel, though it may change upon standing and come toward the false. I would not want to be committed to stating that there is a sharp distinction between true and false gels.

J. ALEXANDER: One point of considerable importance, of course, is viscosity.

H. N. HOLMES: Dr. Weiser has called attention to the importance of the time element in the formation of these threads. I cannot help but think that it is possible in such cases where solvation occurs that the time element of solvation might be a point. I wonder whether it is not possible that the presence of one type of ion may delay the hydration and another type may not delay it.

H. S. TAYLOR: In connection with that remark which you have just made, it has occurred to me that your systems are too complicated for my elementary mind, but if I take a single adsorbing substance and a gas, I find very different velocities of adsorption. Indeed, the rate of attainment of equilibrium in the adsorption of the gas is very largely determined by the purity of the gas or the cleanliness of the surface on which the gas is being adsorbed. When you are dealing with complicated systems of this type it seems to me that the influence of the other combinations must be quite tremendous.

[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY,  
UNIVERSITY OF WISCONSIN]

## COLLOID CHEMISTRY TECHNIQUE

BY THE SVEDBERG

Colloid chemistry originates from Graham's discovery of a new technique for separating substances in solution—from the discovery of dialysis in 1861. The construction of the ultramicroscope by Siedentopf and Zsigmondy in 1903 gave the impetus to the astonishingly rapid development of modern colloid chemistry.

The ordinary methods of chemistry and physics have only a limited bearing upon the colloid systems, because these methods have been developed without taking into account the particular properties, the peculiar structure, of colloids. Almost every advance in colloid chemistry can therefore be traced back to some new technical means especially designed for the study of colloids. Colloid chemistry has been neglected, it has not yet got the experimental equipment that its sister sciences have had at their disposal for quite a while. This undoubtedly is to some extent due to the fact that it has not until recently been fully understood that colloid chemistry requires its own technical facilities, different from the ordinary equipment of a physico-chemical laboratory. We have to contemplate the properties of colloids, as far as we know them, and ask ourselves: what kinds of instruments would one like to have at one's disposal to study such systems? I think that such a method would pay much better in the long run than just to take the instruments one might happen to come across in the field of ordinary physics and chemistry and try to study colloids by means of those instruments. In my opinion it would save a lot of work, time and money if the colloid chemist would stop a moment in his investigations of colloid systems and take a look at his equipment. He would find then that all the technical means we use in colloid chemistry are not rational, that, perhaps, we had better devote some of our time and attention to the development of colloid chemistry technique before we try to proceed any further in our investigations of the colloid systems.

In the following paper the writer will try to outline the col-

loid chemistry technique at our disposal at the present time together with a few suggestions for new methods.

#### PREPARATION OF SOLS

The colloid systems we usually meet with in the products of nature are too complicated to be elucidated at the present time. In order to understand these systems—so very important from a practical point of view—and in order to find out the general laws of colloid chemistry we have to produce artificial systems of the highest possible simplicity and purity, we have to prepare well defined colloids—reproducible colloids.<sup>1</sup>

The material of the disperse phase should be well defined. Sols of elements (metals, sulphur, selenium, carbon), of oxides ( $\text{SiO}_2$ ,  $\text{SnO}_2$ ), of sulphides ( $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ), and of sparingly soluble salts ( $\text{BaSO}_4$ ) have been studied. In some cases dispersion methods, *i. e.*, subdividing of the material down to colloid dimensions, can be used. The colloid mill,<sup>2</sup> devised by Plauson, is a very promising apparatus for subdividing material. Different kinds of substances, especially electrolytes, must be added to prevent coagulation of the fine particles. In most cases the colloid particles are formed by condensation methods, *i. e.*, by condensing atoms or molecules to particles of colloid dimensions. Chemical reactions are often used for producing the material of the disperse phase in a supersaturated molecular state, which must precede condensation to colloid particles.

Most of the elements are metals but only a few metals can be brought to the colloid state of subdivision by chemical reactions. Therefore the method of producing gas of the metal in question by means of the electric arc and condensing the metal gas under the surface of the dispersion medium (water, alcohol, ether, acetone, etc.) has been adopted. Bredig<sup>3</sup> started this line of work by using the free direct current arc in water and the writer and his co-workers have developed methods of preparing metal sols by using a D. C. arc protected from the liquid<sup>4</sup> and by using the high frequency alternating current arc.<sup>1</sup>

<sup>1</sup> Svedberg, "Formation of Colloids," London, 1921; "Herstellung kolloider Lösungen anorganischer Stoffe," Dresden, 1909

<sup>2</sup> See Kenney, *Chem. Met. Eng.*, **27**, 1080 (1922)

<sup>3</sup> Bredig, *Z. angew. Chem.*, 1898, p. 951; "Anorganische Fermente," Leipzig, 1901; *Z. physik. Chem.*, **32**, 127 (1900)

<sup>4</sup> Svedberg, *Medd. Vetenskapsakad. Nobelinstit.*, Stockholm, **5**, No. 10, p. 3 (1919)

The first of the latter two methods works with a D. C. arc burning in a quartz tube provided with a small hole in front of the arc. Pure nitrogen is passed through the quartz tube and the hole of the tube is immersed under the surface of a liquid, *e. g.*, alcohol. The metal gas is carried with the stream of nitrogen and thus blown out into the alcohol where it is condensed to colloid silver. The decomposition of the alcohol by the arc is low because of the protection afforded by the quartz tube. The glowing electrodes do not come in contact with the dispersion medium but only the silver vapor. The sols are contaminated by colloidal  $\text{SiO}_2$  from the tube. Gold, silver and copper sols of a few  $\mu\mu$  diameter of particles can be obtained.

The second method can be applied in different ways depending upon the electrical source available. An oscillatory circuit giving a frequency of not less than about 1,000,000 cycles is built up of a suitable spark gap having electrodes of the metal to be studied and a capacity. In the writer's first experiments the spark gap was connected up to an induction coil. An ordinary low frequency A. C. transformer of about 25,000 volts can be used with success instead of the induction coil. Under certain conditions a D. C. potential as low as 400 or 500 volts can be used for feeding the oscillatory circuit. In certain cases, for instance if the dispersion medium has a comparatively high conductivity, it is better to transfer the oscillations over a transformer from the circuit where they are generated to the circuit where the colloid producing arc is inserted. That is we have to use two high frequency circuits coupled together, one for the generation of the oscillations and one for the preparation of the sol. According to recent investigations by Kraemer and the writer, at Wisconsin, this arrangement also gives purer sols than the other ones.

The purity of the sols prepared by means of the high frequency arc is considerably higher than the purity of those prepared by means of the free D. C. arc. Thus the conductivity of a high frequency A. C. sol is lower than that of the dispersion medium used in preparing it, owing to adsorption of the conducting impurities on the particles, while the conductivity of a sol made by means of the free D. C. arc is higher than that of the dispersion medium. In the latter case

so many impurities have been produced during the colloid producing process that the loss in conductivity by adsorption is more than compensated.<sup>5</sup>

The degree of dispersion of the high frequency A. C. sols is higher than that of the D. C. sols prepared by means of the free arc.<sup>6</sup>

To cut down the decomposition of the dispersion medium and prevent coagulation during formation, a procedure allowing the dispersion medium to stream rapidly through the arc is now being worked out by Kraemer and the writer in the colloid laboratory at Wisconsin.

Another property of the sols necessary in many quantitative investigations is monodispersity, *i. e.*, uniformity in the size of the particles. Most of the processes utilized for the formation of sols lead to systems containing particles of different sizes. In order to obtain sols with particles of equal size, it is necessary either to try to conduct the process of formation so as to give particles of equal size or to separate out particles of equal size from the mixtures of different sized particles.

Zsigmondy has shown that by introducing a certain number of gold nuclei, *i. e.*, small gold particles, in a suitable gold reduction mixture practically all the gold from the molecular solution deposits on those nuclei. The sol formed contains particles of different sizes, but it is more uniform than gold sols prepared by allowing the molecular dissolved gold to deposit on nuclei formed spontaneously during the condensation process.<sup>7</sup>

When a colloid is formed by the reaction between two solutions it is essential that the reaction should be slow enough to allow complete mixing of the reacting solutions before the condensation process sets in. The formation of the particles here takes place simultaneously throughout the whole volume of the system (volume condensation) and the uniform conditions therefore allow the production of a sol with rather equal sized particles.

To select out the different sized particles in a mixture three methods have been used, *viz.*, fractional diffusion, fractional

<sup>5</sup> Nordlund, "Quecksilberhydrosol," Diss. Upsala, 1918, p. 86

<sup>6</sup> Börjeson, "Electric Synthesis of Colloids," Diss. Upsala, 1920

<sup>7</sup> Zsigmondy, *Z. physik. Chem.*, **86**, 65, 77 (1906)

sedimentation or centrifuging, and fractional coagulation. The first method has been tried by Dabrowski in the case of proteins<sup>8</sup> but has not led to any definite results. Fractional sedimentation has been used by Westgren<sup>9</sup> for making coarse grained gold sols more uniform in size. Fractional centrifuging was used by Perrin for preparing monodisperse gamboge and mastic sols.<sup>10</sup> A difficulty with the centrifugal method is that the particles centrifuged down to the bottom of the tube are pressed together so firmly that they often coalesce.

Fractional coagulation has been applied with great success by Odén in the case of silver sols and sulphur sols.<sup>11</sup> Odén showed that in both these cases the coarse particles were more sensitive to electrolytes than the small ones. For silver sols ammonium nitrate, and for sulphur sols sodium chloride were used as coagulants.

#### PURIFICATION OF SOLS

For the removal of certain undesirable ions coagulation with some other less objectionable electrolyte and redissolving of the coagulum can be used. In some cases, *e. g.*, silver, part of the electrolytes present can be removed by coagulation with alcohol.

Graham's classical method of separating colloids and crystalloids, dialysis, is still the most important procedure of purification.<sup>12</sup> The membranes mostly used now are collodion films. They can be prepared in different thicknesses and with pores of different size by varying the concentration of the collodion solution and the proportions of alcohol and ether in it. Flowing water should be used and a large diffusing surface arranged for.<sup>13</sup> In the case of substances apt to undergo hydrolysis, *e. g.*, proteins, the dialyzer should be enclosed in a refrigerator to keep the temperature down.<sup>14</sup> An arrangement for saturating the water with toluene before it enters the dialyzer is to be recommended for proteins in order to prevent bacterial decomposition.

<sup>8</sup> Dabrowski, *Bull. intern. acad. sci. Cracovie, Classe math. et nat., A, Juin, 1912*

<sup>9</sup> Westgren, "Die Brownsche Bewegung," Diss. Upsala, 1915

<sup>10</sup> Perrin, *Ann. chim. phys.*, [8] **18**, 5 (1909)

<sup>11</sup> Odén, *Z. physik. Chem.*, **78**, 682 (1912)

<sup>12</sup> Graham, *Trans. Roy. Soc. London*, **151**, 183 (1861)

<sup>13</sup> Zsigmondy and Heyer, *Z. anorg. Chem.*, **68**, 169 (1910)

<sup>14</sup> Sørensen, *Medel. Carlsberg Lab., Kjöbenhavn*, **12**, 25 (1917)



Ultrafiltration has been used for purifying sols.<sup>15</sup> Pure water is continually pressed through the sol. Collodion membranes, *e. g.*, in the form of bags, give the best results. In some cases ultrafiltration works faster than dialysis, but many sensitive sols do not stand the concentration of the particles at the bottom of the filtration bag.

Electrodialysis is a comparatively new method which seems to be more efficient than dialysis. The electrodes are separated from the sol by membranes which prevent the particles going through. From time to time the contents of the electrode vessels are removed and pure water poured in. Odén has prepared very pure sulphur sols by such a procedure<sup>16</sup> and in the Eastman Kodak Research Laboratory gelatin has been purified in this way.

As yet we do not know of any suitable membranes to be used for purifying organosols by dialysis, ultrafiltration or electrodialysis. It would be of importance to undertake a systematic search for such membranes. Some preliminary experiments by Pope and the writer indicate that the task is not at all hopeless.

Sedimentation was used by Westgren for purifying coarse grained gold sols. The particles were allowed to settle, the supernatant liquid siphoned off and replaced by pure water. The same method can be used in centrifuging, but here we meet with the difficulty that the particles often coalesce when centrifuged down to the bottom. It may be possible to eliminate this effect by choosing a suitable material for the particles to rest upon.

#### DETERMINATION OF SIZE, SHAPE AND STRUCTURE OF PARTICLES

The classical method of determining the size of particles in sols as worked out by Siedentopf and Zsigmondy is by means of the ultramicroscope.<sup>17</sup> A small volume of the sol enclosed in a suitable cell is illuminated intensely and the number  $n$  of particles in this small volume made visible by the light they emit when illuminated are counted. If we know the mass  $M$  of the disperse phase in this volume we can find the mass of a single particle and assuming that the density  $\rho$  is the same as

<sup>15</sup> Malfitano, *Compt. rend.*, **139**, 1221 (1904); Duclaux, *Compt. rend.*, **140**, 1468, 1544 (1905); Bechhold, *Z. physik. Chem.*, **60**, 257 (1907)

<sup>16</sup> Odén, *Nova Acta, Upsala*, [4] **3**, No. 4, p. 66 (1913)

<sup>17</sup> Siedentopf and Zsigmondy, *Ann. Physik.*, [4] **10**, 1 (1903)

in the macroscopic material, we have in the case of spherical particles.

$$r = \sqrt[3]{\frac{3M}{4n\pi\rho}}$$

where  $r$  is the radius of the particle.

The problem of illuminating the particles as intensely as possible has been solved in different ways. The slit ultramicroscope devised by Siedentopf and Zsigmondy has the illuminating and observing beams at right angles and so has also the immersion ultramicroscope devised by Zsigmondy.<sup>18</sup> In the latter instrument the aperture of the illuminating system and the aperture of the lens used for observing the particles is considerably higher than in the slit ultramicroscope. The limit of visibility is therefore somewhat lower down in the region of the small particles. On the other hand the immersion ultramicroscope is less easy to manipulate. The illuminating and observing lenses are so close together that it is difficult to arrange for a suitable cell to hold the sol under investigation.

Another class of ultramicroscopes, the so-called dark field condensers, have the illuminating and observing beams coaxial but either utilize different apertures so that no direct rays from the illuminating system can enter the lens of observation, or are constructed so that the rays of illumination are totally reflected at the upper surface<sup>19</sup> of the cover-glass. One of the most perfect instruments among these dark field condensers is the Zeiss cardioid condenser devised by Siedentopf.<sup>19</sup>

The dark field condensers give a more intense illumination than the ultramicroscopes with orthogonal illumination. They are especially useful for photographing the particles. The background against which the particles are seen is however less dark than with the slit ultramicroscope and the immersion ultramicroscope and therefore in case of direct ocular examination we often find this decreased contrast objectionable. Another drawback is that for observations with a dark field condenser the sol must be enclosed in a very thin cell. The influence of the walls of the cell is therefore often noticeable. Siedentopf tried to diminish this source of error by using cells of fused quartz.

<sup>18</sup> Zsigmondy, *Physik. Z.*, **14**, 975 (1913); "Kolloidchemie," **1920**, p. 12

<sup>19</sup> Siedentopf, *Verhandl. physik. Ges.*, **12**, 1 (1910)

In cases where the particles are too small to be counted in the ultramicroscope it is possible to deposit gold around them thus making them large enough to be seen and counted. This method was first used by Zsigmondy<sup>7</sup> in the case of invisible, or so-called amicroscopic gold particles. Börjeson showed that the same procedure can be applied to all kinds of metallic particles and even to some sulphide particles.<sup>20</sup> As reduction mixture chlorauric acid and hydrogen peroxide is usually used. Westgren determined the limits of concentration of gold salt and of the number of nuclei within which the method is reliable.<sup>21</sup> The point is of course that there should take place no spontaneous formation of gold nuclei from the reduction mixture but that all the molecular gold should be deposited upon the nuclei introduced. In the case of organosols, successive dilutions with suitable liquids enable us to use the same method. If we desire to measure the size of small metallic particles in ether we first dilute this sol with alcohol and then a portion of the new sol with water.

It is difficult to get information about the different sizes of particles in a sol by observations in the ultramicroscope. The varying brightness of the particles seen gives us some idea of sizes but no definite values can be arrived at by such observations.

Observations in the ultramicroscope, especially when illuminating with linearly polarized light at right angles to the axis of observation, can give information about the shape of the particles. Twinkling light from the particles indicates dissymmetry.

A series of important methods of studying the size of particles and the distribution of sizes of particles in sols are based upon measurements of the frictional force which is brought into action when the particle moves under the influence of some force. If the particle is spherical with radius  $r$  and moves with the velocity  $v$  in a medium with the viscosity  $\eta$  the frictional force  $f$  is:

$$f = 6\pi\eta rv$$

By measuring  $f$ ,  $\eta$  and  $v$  we are able to calculate  $r$ . In

<sup>20</sup> Börjeson, *Kolloid-Z.*, **27**, 18 (1920)

<sup>21</sup> Westgren, "Die Brownsche Bewegung," Diss. Upsala, 1915, p. 68

cases where the particles are not spherical the value of  $r$  which we obtain in this way is the radius of a particle equivalent to the particle studied with regard to the frictional force exerted against it.

If the difference in density between particle and liquid is great enough and the particle rather large we can use the force of gravity to move the particle, *i. e.*, we can observe the rate of sedimentation. When constant velocity is reached the force of gravity equals the force of friction, from this equality we get the well-known Stokes formula:

$$r = \sqrt{\frac{9\eta x}{2(\rho_p - \rho_d)gt}}$$

Measurement of the viscosity of the medium  $\eta$ , the height of fall  $x$ , density of the particle  $\rho_p$ , the density of the dispersion medium  $\rho_d$ , the gravity constant  $g$ , and the time of fall  $t$  enables us to calculate the "equivalent radius"  $r$  of the particle.

The quantities  $x$  and  $t$  can be observed in the ultramicroscope. If the sol contains particles of different size we can measure the rate of fall of a large number of particles and from those values derive the distribution curve giving the relation between radius and relative number or relative mass of particles within a certain radius interval. Such curves were first presented by Estrup and the writer.<sup>22</sup>

Instead of measuring directly in the ultramicroscope the rate of fall of the particle one can take photomicrographs of the paths of the particles and measure those.

The rate of sedimentation can also be observed macroscopically by measuring the movement of the boundary between sol and clear dispersion medium under the influence of gravity. Calculations of the radius of the particle from such observations give us the minimum size of particles in the sol studied.

In some cases, *e. g.*, when studying small metallic particles, which do not settle under the influence of gravity, we can increase the size by depositing gold upon them and then measure the radius of such gilded particles by means of the rate of fall. The size of the original particles can then be calculated.

Besides the rather tedious procedure of measuring directly in the ultramicroscope the rate of fall of a large number of

<sup>22</sup> Svedberg and Estrup, *Kolloid-Z.*, 9, 259 (1911)

particles and calculating the distribution curve from those measurements we have two other methods of recording the distribution of sizes of particles in a coarse grained disperse system.

In one of them the rate of accumulation of sediment is measured by means of a self-recording balance (Odén) and in the other the concentration of the sol as a function of height is measured during sedimentation (Rinde and the writer).

Odén has used the first method with great success for recording the size distribution of clays and precipitates.<sup>23</sup> The distribution function  $\frac{dS}{dr}$ , where  $dS$  is the percentage mass of particles corresponding to the radius interval  $dr$ , is related to the rate of accumulation  $\frac{dP}{dt}$  in the following way:

$$\frac{dS}{dr} = - \frac{2t^2}{r} \cdot \frac{d^2P}{dt^2}$$

By means of this relation or by a graphical method the distribution function can be found.

The second procedure was used by Rinde and the writer for the study of gold sols.<sup>24</sup> If the concentration at different heights is determined by means of light absorption measurements we have

$$\frac{dS}{dr} = \frac{2\sqrt{x}}{k_1 \sqrt{\frac{9\eta}{2(\rho_p - \rho_d)gl}}} \cdot \frac{dk}{dx}$$

where  $k$  is the light absorption constant measured and  $k_1$  the same constant for unit concentration. If the light absorption varies with size of particles as is often the case, the values of  $k_1$  have to be taken from an experimentally determined diagram giving the relation between  $k_1$  and the radius. By combining methods one and two, i. e., by recording both the rate of accumulation and the variation of light absorption with height it is possible to calculate the light absorption constant as a function of the radius.

Most sols have particles too small to allow determinations of size of particles by utilizing the force of gravity. Recently

<sup>23</sup> Odén, *Proc. Roy. Soc. Edinburgh*, **36**, 219 (1916); *Int. Mitt. Bodenk.*, **1915**; *Bull. Geol. Inst., Univ. Upsala*, **16**, (1916)

<sup>24</sup> Svedberg and Rinde, *J. Am. Chem. Soc.*, **45**, 943 (1923)

the writer has suggested the use of a centrifugal force in such cases where settling under the influence of gravity is too slow.

The frictional force is here  $6\pi\eta \frac{dx}{dt}$  and the centrifugal force  $4/3\pi r^3(\rho_p - \rho_d)\omega^2 x$  where  $\omega$  is the angular velocity and  $x$  the distance between the particle and the axis of revolution. These forces must be equal; integration then gives us

$$r = \sqrt{\frac{9\eta(\ln x_2 - \ln x_1)}{2(\rho_p - \rho_d)\omega^2 t}}$$

where  $x_1$  is the position of the particle at the time zero and  $x_2$  the position of the particle at the time  $t$ .

Nichols and the writer (in this laboratory) have carried out measurements of size of particles in fine grained sols by using a special centrifuge which allowed determinations of the movement of the boundary between the sol and the clear dispersion medium during centrifuging. This method is now being worked out more in detail and seems to be rather promising. In some cases we have already been able to measure the size of particles which could not be counted in the ultramicroscope. In cases where both the centrifugal and the ultramicroscopic method could be applied the values found by the different methods agreed very well.

The centrifugal method can also be used for recording the distribution curve of fine grained sols. The experimental details are now being worked out by Nichols and the writer. Photographs of the sol during centrifuging are taken and from measurements on the plates the variation of light absorption with distance from the axis of revolution can be calculated. Our distribution function is given by the following expression:

$$\frac{dS}{dr} = \frac{2x_2\sqrt{\ln x_2 - \ln x_1}}{k_1 \sqrt{\frac{9\eta}{2(\rho_p - \rho_d)\omega^2 t}}} \cdot \frac{dk}{dx}$$

The frictional force enters into all the different laws of the Brownian movement.<sup>25</sup> Measurements of the displacement of the particle under the influence of the Brownian movement and measurements of the velocity of fluctuation of the number of particles within a small volume of the sol can be used for cal-

<sup>25</sup> See Einstein, *Ann. Physik.*, [4] 17, 549 (1905); Smoluchowski, *Ann. Physik.*, [4] 21, 756 (1906); *Physik. Z.*, 17, 557 (1916)

culations of the radius. If  $\overline{\Delta^2}$  is the average square of the displacement during a certain time  $t$  we have

$$r = \frac{RT}{N} \cdot \frac{1}{3\pi\eta\overline{\Delta^2}}$$

where  $R$  is the gas constant,  $T$  the absolute temperature and  $N$  the Avogadro constant.

This relation has actually been used for determination of size of particles in gases. Estrup and the writer suggested the use of such measurements for the calculation of distribution curves<sup>22</sup> but owing to the large number of measurements necessary for the construction of a single distribution curve the method has never been tested experimentally.

Measurements of fluctuations have not yet been used for the study of the size of the particles.

The frictional force as displayed in diffusion is easier to measure. We have

$$r = \frac{RT}{N} \cdot \frac{1}{6\pi\eta D}$$

where  $D$  is the diffusion constant. The size of particles in fine grained gold sols have been measured in this way by the writer and by Westgren. Herzog<sup>26</sup> and Dabrowski<sup>8</sup> have used the method for the study of the particles in protein sols.

It is possible to build up a method for recording distribution curves from observations of diffusion. The simplest case is when the thickness of the layer of the sol is small compared with the thickness of the pure dispersion medium on top of it. We have for the concentration  $c$  of the disperse phase at a certain distance  $x$  from the bottom

$$c = \frac{\text{const.}}{t} \sum_{k=1}^n \frac{c_k}{\sqrt{D_k}} e^{-\frac{x^2}{4D_k t}}$$

where  $t$  is the time of diffusion,  $c_k$  the initial concentration of the part of the sol with the diffusion constant  $D_k$ . If a sufficient number of determinations were made at different heights and at different times it would be possible to calculate  $c_1 c_2 \dots c_k$  and  $D_1 D_2 \dots D_k$  and from those data, the distribution

<sup>26</sup> Herzog, *Z. Elektrochem.*, **13**, 533 (1907); Herzog and Polotzsky, *Z. physik. Chem.*, **87**, 449 (1914); *Z. Elektrochem.*, **17**, 679 (1911)

curve. Experiments of this kind are planned in the writer's laboratory. They are of importance because we are here dealing with one of the few possible means for studying the distribution of sizes in protein sols.

The formula for the osmotic pressure  $p$  of a sol offers a possibility of counting the number  $n$  of particles per unit volume. We have

$$n = \frac{Np}{RT}$$

There are, however, many sources of error in measurements of osmotic pressure of sols. The pressures are often very low because of the small number of particles per unit volume and the osmotic pressure exerted by the crystalloids present complicate the phenomenon. By means of the Donnan equilibrium formula, these influences can be taken into account as far as the electrolytes are concerned.<sup>27</sup>

The size and shape of the particles can be computed from measurements of light absorption and the Tyndall effect.<sup>28</sup> The relationship between size or shape and light absorption constant or light emission are however rather complicated.<sup>29</sup> It is therefore advisable to use experimentally determined graphs giving these relations instead of calculating them from theoretical formulae. If possible the measurements should be arranged so that the absorption and the scattering of light could be measured on the same sol. A method of this kind is in use in the writer's laboratory. The quartz spectrograph of high aperture can be brought into two positions: (1) in the axis of the illuminating beam for measuring the absorption and (2) orthogonal to the illuminating beam for measuring the scattered light.

Freundlich has shown that studies of the intensity of the scattered light is a means of getting some information about the shape of the particles.<sup>30</sup> If the sol is allowed to stream through a cell of rectangular cross-section, dissymmetrical

<sup>27</sup> Sorensen, *Meddel. Carlsberg Lab.*, Kjöbenhavn, **12**, 255 (1917)

<sup>28</sup> Svedberg, "Die Existenz der Moleküle," Leipzig, 1912, p. 5, Pihlblad, "Lichtabsorption und Teilchengrösse," Diss., Upsala, 1918; Mecklenburg, *Koll.-Z.*, **16**, 97 (1915)

<sup>29</sup> Mie, *Ann. Physik.*, [4] **25**, 377 (1908); Rayleigh, *Phil. Mag.*, [5] **47**, 377 (1899); Maxwell-Garnett, *Phil. Trans. Roy. Soc. London*, **203A**, 385 (1904); **205**, 237 (1906)

<sup>30</sup> "Kapillarchemie," Leipzig, 1922, p. 552; Freundlich and Diesselhorst, *Physik. Z.* **17**, 117 (1916)



particles are oriented, *viz.*, needle-shaped particles with their axis parallel to the direction of flow and leaf-shaped particles with their planes parallel to the broadest side of the cell. By illuminating the streaming sol with linear polarized light at different directions and observing the intensity of the scattered light it is possible to distinguish between needle-shaped and leaf-shaped particles.

A still more sensitive means of detecting dissymmetry in the particles is by measuring the double refraction of the sol induced by a magnetic or electric field. The magnetic field especially is convenient to use because it causes no electrolysis and has no coagulating effect. Björnsthål has studied the phenomenon of double-refraction in different sols and found that in most sols deviations from the spherical shape can be detected and measured. The formation and the coagulation of a sol can be followed by such measurements.<sup>31</sup>

The X-ray analysis has been utilized in the study of the inner structure of the particles of sols and gels by Scherrer.<sup>32</sup> The ordinary Debye-Hull apparatus is used. Difficulties arise from the strong coagulating action of the X-rays on the sol. It is therefore sometimes necessary to allow the sol to stream through the camera during exposure (Björnsthål). Only a few measurements of this kind have been carried out so far, but this method will doubtless prove to be of considerable value for the elucidation of the structure of the particles.

It is interesting to note that according to some theoretical considerations by Scherrer it is possible to estimate the size of very small particles from measurements of the width of the lines on the X-ray spectrograms, provided we know the wave length of the rays used and the crystal lattice of the particles. In the case of a cubic lattice he gives the formula

$$a = 2\sqrt{\frac{2}{\pi}} \cdot \frac{\lambda}{W} \frac{1}{\cos \varphi}$$

where  $a$  is the linear dimension of the particles and  $\varphi$  the angle between the ray and the planes of the crystal. Values of the size of the particles arrived at by this method and by measuring the osmotic pressure show a rather striking agreement.

<sup>31</sup> Björnsthål, *Phil. Mag.*, [6] 42, 352 (1921)

<sup>32</sup> Scherrer in Zsigmondy, "Kolloidchemie," Leipzig, 1920, p. 387

## MEASUREMENT OF CATAPHORESIS AND MOBILITY OF PARTICLES

The cataphoresis can be measured either directly by following the movement of the single particle in the ultramicroscope or by following the movement of a boundary between sol and dispersion medium. The first method is more reliable than the second one. The use of a boundary necessarily involves a certain discontinuity in the electric field acting upon the particles and the mobilities calculated from such measurements are therefore less well defined.

Ultramicroscopic studies of cataphoresis were first carried out by Cotton and Mouton.<sup>33</sup> Andersson and the writer have worked out a procedure based upon the use of a dark field condenser such as the cardioid condenser.<sup>34</sup> The sol to be studied is enclosed in a thin cell provided with electrodes of platinum foil. An alternating current generated by a special commutator is used and the tracks of the particles measured by means of a scale in the ocular. Observations are made at different points between the walls of the cell in order to eliminate the influence of endosmosis. If the potential curve of the commutator is known the mobility can be calculated from determinations at two different distances from the wall by means of formulae deduced by Smoluchowski,<sup>35</sup> e. g., from determinations at  $1/6$  and  $1/2$  the distance between the walls. In this particular case we have for the absolute velocity  $u$  of the particle

$$u = \frac{3}{4}u'_{1/6} + \frac{1}{4}u'_{1/2}$$

where  $u'_{1/6}$  and  $u'_{1/2}$  mean the observed velocity of the particle at  $1/6$  and  $1/2$  the distance between the walls respectively.

Cataphoresis cells for the slit ultramicroscope have been devised by the writer<sup>36</sup> and by Kruyt.<sup>37</sup> The latter has recommended the use of suitable reversible electrodes to prevent the accumulation of products of electrolysis.

Many sols have particles too small or of too low light reflecting power to be seen in the ultramicroscope. In such cases observations on a boundary between sol and dispersion

<sup>33</sup> Cotton and Mouton, *Compt. rend.*, **138**, 1504 (1904)

<sup>34</sup> Svedberg and Andersson, *Kolloid-Z.*, **24**, 156 (1919)

<sup>35</sup> Smoluchowski, in Graetz "Handbuch d. Elektrizität u. Magn.," Leipzig, **1914**, vol. 2, p. 382

<sup>36</sup> Svedberg, *Nova Acta, Upsala*, [4] **2**, No. 1, p. 149 (1907)

<sup>37</sup> Kruyt and van Arkel, *Kolloid-Z.*, **32**, 91 (1923)

medium must be made. A U-tube provided with a narrow tube sealed in at the lowest point of the U is often used for the measurement of cataphoresis. The sol to be studied is run down slowly through the narrow tube under a layer of the pure dispersion medium. The electric field is applied by means of two electrodes dipped into the dispersion medium at the ends of the U. Platinized platinum electrodes or reversible electrodes of different kinds have been used.

This type of the U-tube method as worked out by Burton,<sup>38</sup> Coehn,<sup>39</sup> Michaelis<sup>40</sup> and others can be used only with colored sols, where the boundary is clearly visible. Many sols, *e. g.*, the proteins, are colorless in dilute solution so that we can hardly see any boundary between the sol and the pure dispersion medium. Jette,<sup>41</sup> Scott and the writer have worked out a procedure for measuring cataphoresis based upon the fluorescence which many colorless substances, *e. g.*, the proteins, show when illuminated with ultraviolet light. A suitable U-tube apparatus provided with reversible Zn-ZnSO<sub>4</sub> electrodes is used. The U-tube is illuminated with ultraviolet light and the position of the boundary as indicated by the fluorescence is recorded from time to time by taking photographs.

#### STUDY OF THE SOLVATION OF THE PARTICLE

The thickness of the layer of dispersion medium adsorbed around the particle is of importance in many colloid phenomena.<sup>42</sup> We possess no direct methods for the study of this quantity but measurements of viscosity<sup>43</sup> and measurements of density of sols can be used for estimating the degree of solvation. The viscosity increases with increasing solvation and so does the density of the sol.

The viscosity is usually measured by means of an ordinary Ostwald viscosimeter. It is often found however that the values obtained vary with the velocity of flow through the tube of the viscosimeter.<sup>44</sup> Special viscosimeters for the study

<sup>38</sup> Burton, *Phil. Mag.*, [6] 11, 436 (1906)

<sup>39</sup> Coehn, *Z. Elektrochem.*, 15, 653 (1909)

<sup>40</sup> Michaelis, *Biochem. Z.*, 16, 81 (1908)

<sup>41</sup> Svedberg and Jette, *J. Am. Chem. Soc.*, 45, 954 (1923)

<sup>42</sup> Zsigmondy, "Kolloidchemie," Leipzig, 1920, p. 97; Kruyt, *Kolloid-Z.*, 20, 239 (1917); Pauli, "Colloid Chemistry of the Proteins," 1922, p. 11

<sup>43</sup> Hatschek, *Kolloid-Z.*, 11, 280, 284 (1912)

<sup>44</sup> Hatschek, *Kolloid-Z.*, 13, 88 (1913)

of sols have therefore been devised allowing measurements at different rates of flow in the sol. An instrument of this kind is the Couette viscosimeter.<sup>45</sup> The sol to be studied is placed in a cylindrical vessel which can be kept in rapid motion by means of a motor. A second cylinder concentric with the former is suspended on a wire and immersed in the sol. The viscosity can be calculated from the angle of rotation of the suspended cylinder. An improved modification of Couette's instrument has been devised by Sheppard.<sup>46</sup>

For measurements of density a sensitive pycnometer can be used. The Sprengel-Ostwald type is perhaps the most convenient one. By means of this method Stein and the writer have studied the change in the hydration of gelatin particles with change in concentration of hydrogen ion and other electrolytes and non-electrolytes present in the sol.

#### STUDY OF COAGULATION

Coagulation is a time phenomenon. The best way of describing coagulation is therefore to determine the number of single particles and the number of the different kinds of aggregates present in the sol at different times under various conditions.<sup>47</sup> The most direct way is to count the particles in the ultramicroscope. If the velocity of coagulation is high the number of particles present at different times after addition of the coagulant has to be determined in different samples of the sol. In each sample the coagulation is broken off by the addition of an efficient protective colloid, e. g., gelatin in the case of a gold sol. This procedure was introduced by Zsigmondy and his co-workers Westgren and Reitstötter.<sup>48</sup>

It is difficult to distinguish between the different kinds of aggregates. Zsigmondy succeeded in counting in the ultramicroscope the primary or single particles in a coagulating gold sol, distinguishing them by their color. The primary particles emitted green light, the aggregates yellow light. This case is however an exception. As a rule the counting in

<sup>45</sup> Couette, *Ann. chim. phys.*, [5] **21**, 433 (1890)

<sup>46</sup> Sheppard, "Gelatin in Photography," **1923**, p. 196

<sup>47</sup> Zsigmondy, *Nachr. Ges. Wiss. Göttingen*, **1917**, p. 1; *Z. physik. Chem.*, **92**, 600 (1917); Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917)

<sup>48</sup> Westgren and Reitstötter, *Z. physik. Chem.*, **92**, 750 (1917); *Jour. Phys. Chem.*, **26**, 537 (1922); Westgren, *Arkiv Mineral. Geol. Kemi*, **7**, No. 6 (1918)

the ultramicroscope only gives us the total number of particles.

Odén<sup>49</sup> has studied coagulation of coarse grained sols by measuring the distribution of the size of the particles by means of his self-recording sedimentation balance. In the case of fine grained sols the centrifugal method for recording distribution curves as suggested by the writer could be used.

Measurements of some property dependent on the number, the size or the shape of the particles in a sol have also been used for the study of coagulation. Such properties are: osmotic pressure, viscosity, light absorption, Tyndall effect and double refraction. The relation between the effect observed and the number of particles in the coagulating sol is, however, rather complicated so that in most cases it is almost impossible to draw any definite conclusions as to the velocity of coagulation from such measurements. The most reliable method would be the measurement of osmotic pressure if the osmotic effects of the electrolytes present could be properly accounted for.

Coagulation is accompanied by a certain, although usually very slight heat effect. It is of importance to know the exact values of these effects. The heat of coagulation has been successfully measured by J. H. Mathews and co-workers<sup>50</sup> by means of the refined calorimetric technique introduced by Richards and adapted by Mathews.

#### STUDY OF THE FORMATION AND PROPERTIES OF GELS

The technique for the study of gels is much less completely developed than the technique for the study of sols.<sup>51</sup> The high importance of gels in many different branches of industry and in biology makes it highly desirable that such methods should be worked out. It is to be hoped that the attempts of the colloid scientists in this direction will soon furnish the means we are looking for.

The formation of a gel has been followed by measuring the viscosity, the degree of rigidity, the elasticity, etc. In many cases however the methods used have been of such a kind as to interfere seriously with the process of gel formation. Viscosity, rigidity and elasticity tests are usually made under such conditions that the gel formation is prevented to some extent or

<sup>49</sup> Odén, *Arkiv Mineral. Geol. Kemi.*, 7, No. 26 (1920)

<sup>50</sup> Browne and Mathews, *J. Am. Chem. Soc.*, 43, 2336 (1921)

<sup>51</sup> Cf. Freundlich, "Kapillarchemie," Leipzig, 1922, p. 905

the gel formed destroyed. The system studied must be handled with care. The writer has suggested that the formation of gels could be studied by quantitative measurements of the Brownian movements of ultramicroscopic particles, *e. g.*, gold or mercury particles, introduced into the system before the gel formation process begins. Measurements of this kind are now in preparation.

The structure of gels can in a few cases be studied with the ultramicroscope but as a rule the structure is so fine and the light emitting power of the material so low that the ultramicroscope does not reveal anything about the structure.<sup>52</sup> Studies of the Brownian movements of foreign particles in the gel and studies of the change in distribution of such particles might be of considerable value for the elucidation of the structure of gels. The study of macro- and especially micro-diffusion in gels and a micro-study of the Liesegang phenomenon is also a promising way of attack.

The swelling of gels has been studied along different lines. The amount of dispersion medium taken up can be measured by means of an apparatus devised by Zsigmondy which allows the experimenter to expose the gel to be studied to the vapors of the dispersion medium at different pressures.<sup>53</sup> A diagram giving the relation between the concentration of the gel and the vapor pressure of the dispersion medium is a valuable characteristic of the gel.

The swelling pressure can be measured by means of the Posnjak apparatus.<sup>54</sup> A tube is closed at one end by a plate of porous porcelain dipping into a beaker containing the dispersion medium. The gel is fixed in the tube on top of the porcelain plate and mercury poured in to fill the tube and part of a capillary connected to the tube. The other end of the tube is closed and the capillary connected up to a manometer and a source of pressure, *e. g.*, a container of compressed air. By regulating the air pressure the swelling pressure can be balanced and measured.

Measurements of elasticity of gels are of importance because of the relation existing between elasticity and structure. Especially the study of the elastic properties of extremely weak

<sup>52</sup> Zsigmondy, *Physik. Z.*, **14**, 1098 (1913)

<sup>53</sup> Zsigmondy, Bachmann and Stevenson, *Z. anorg. Chem.*, **75**, 189 (1912)

<sup>54</sup> Posnjak, *Kolloidchem. Beihfte*, **3**, 417 (1912)

gels would be of considerable importance for the understanding of the formation and structure of gels. The methods in use at the present time allow us to measure the elasticity only of comparatively rigid gels.

A procedure that has been used by Rohloff and Shinjo<sup>55</sup> and in a modified form by Kraemer and the writer is the following. The gel to be studied is enclosed between two concentric spheres one of which is fixed and the other suspended on a wire or on a bifilar suspension. The angle of rotation  $\varphi$  of the sphere corresponding to a certain angle of torsion  $\theta$  of the suspension is measured. For the elasticity modulus  $E$  we have

$$E = \frac{mgab}{4\pi l R_i^3} \left(1 - \frac{R_i^3}{R_o^3}\right) \frac{\sin \theta}{\varphi}$$

where  $a$  and  $b$  are the distances between the upper and lower ends and  $l$  the lengths of the bifilar suspension wires,  $g$  the gravity constant,  $m$  the apparent weight of the sphere,  $R_i$  and  $R_o$  the radius of the inner and the outer sphere respectively.

If a sphere is suspended in an unlimited liquid, which is approximately the case with a small sphere of radius  $R$  immersed in a big beaker filled with gel, the above formula can be simplified to.

$$E = \frac{mgab}{4\pi l R^3} \frac{\sin \theta}{\varphi}.$$

Freundlich and Seifriz<sup>56</sup> have worked out a micro method for the study of the elastic properties of gels. A nickel globule of say  $10 \mu$  diameter is introduced into the gel by means of a couple of fine glass needles and the nickel globule observed under the microscope when exposed to the action of a non-homogeneous magnetic field from a special electromagnet provided with a needle shaped pole forced into the gel. From the displacement of the nickel globule the elastic properties of the gel can be calculated. A drawback of this otherwise very promising method is that the introduction of the nickel particle destroys the gel structure to a certain extent.

<sup>55</sup> Rohloff and Shinjo, *Physik. Z.*, **8**, 442 (1907)

<sup>56</sup> Freundlich and Seifriz, *Z. physik. Chem.*, **104**, 233 (1923)

DISCUSSION ON T. SVEDBERG'S PAPER  
DEMONSTRATIONS OF COLLOID CHEMISTRY  
TECHNIQUE

N. E. GORDON: On the preparation of this last, I was wondering how high a concentration you could get. Also you describe ether as a medium, and you spoke about alcohol. We tried using alcohol and found that we got more carbon than anything else. I was wondering if you were trying to get a high concentration of calcium.

T. SVEDBERG: The diagram showing the relative pulverization of metals referred to the preparation in ether, but all those sols cannot be had at a very high concentration. Some of the other metals, for instance, cadmium, can be prepared in higher concentration, but I do not think it is possible to produce calcium sols in any high concentration.

J. ALEXANDER: I would like to ask whether that is not due to the fact that in the majority of the cases the particles that are being examined are not small particles but are in themselves complexes? For instance, you can take a gum and let it soak up in water, and then take that same gum and partially dehydrate it and you will find that although the particles may be the same (the number of them), the particles will be swelled to a very different degree.

T. SVEDBERG: That is true, but such particles have not yet been studied very much. Most of them cannot be seen in the ultramicroscope. But if we knew anything about the density, the radius of those particles could of course be determined.

E. B. SPEAR: I am sorry that I have to interrupt with a question, but I did not quite understand what you said, Prof. Svedberg, toward the last, though you probably have covered it. How small may the particles be before the precipitation or settling methods become unreliable? For instance, if we have very fine gold particles the method does not hold at all, but on very large particles it is quite reliable. How small, approximately, may these particles be before we get very erroneous results?

T. SVEDBERG: In the case of a heavy particle such as gold in water, we can apply the Stokes method and get the distribution curve down to particles of about 80  $\mu\mu$  in radius, but



for substances with lower density the limit will be determined by the specific gravity.

MR. ———: I would like to know if you have any tentative suggestion for the cause of formation of the Liesegang rings.

T. SVEDBERG: I think those so far proposed are all unsatisfactory. I do not think anyone can explain the phenomenon. Perhaps by measuring the electrolytic conductivity and by studying the light adsorption or other physical properties of that kind we will be able to follow the changes in concentration better than we have been able to do so far. We do not know now anything at all about the changes in concentration that take place, and I think that we ought to do that before we can possibly get any reliable theory.

E. F. BURTON: I did not understand how Professor Svedberg measured the cataphoresis of the particles under the ultramicroscope.

T. SVEDBERG: We used an alternating current produced by a commutator in order to avoid electrolysis. In the field of the microscope we get streaks of light as already observed by Cotton and Mouton in the case of an ordinary alternating current. We measured the length of these lines and knowing the length of time during which the current is closed we computed the mobility of the particles. We have also used direct current for operating for a short time, but we obtained better results with the other means.

R. A. GORTNER: How long is it between alternations?

T. SVEDBERG: I do not exactly remember. We used a very low frequency.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY  
OF PRINCETON UNIVERSITY]

## THE PROBLEM OF ADSORPTION FROM THE STAND- POINT OF CATALYSIS

BY HUGH S. TAYLOR

In a discussion of the adsorption of gases at solid surfaces more especially with regard to the Langmuir theory of adsorption, Freundlich<sup>1</sup> points out that "one might ask, why on the basis of the Langmuir theory, adsorption is so little specific, if it were not true that the number of adsorbents thoroughly studied is not yet large." Classical colloid chemistry has been concerned with adsorption by relatively few adsorbents. The study of adsorption from the standpoint of contact catalysis extends enormously the range both of adsorbents and adsorbates.<sup>2</sup> Such extension of the field of study shows that adsorption is a much more inclusive term than formerly believed. It embraces not only physical, capillary condensation phenomena, non-specific in character and paralleling the physical characteristics of the adsorbate but also definite associations between adsorbent and adsorbate, specific and chemical in character, independent of the physical characteristics of the adsorbate and similar in every respect to ordinary compound formation in stoichiometric proportions. It is these latter adsorptions which are more important in contact catalysis; the former have been discussed almost exclusively in colloid texts.

An index of the range of adsorption is obtained by a study of "poisoning" in contact catalysis. For, such cases are to be attributed frequently to adsorption, on the catalyst surface, of a constituent of the surrounding phase which is present only in minute quantities and which is held by the adsorbent so tenaciously that it is with difficulty removed. Certain cases of poisoning are not due to adsorption but to actual chemical reaction with the catalyst resulting in modification of the chemical nature of the catalyst. The problem of poisoning has been treated very comprehensively in recent years and has received quantitative study.<sup>3</sup> It will only be necessary, therefore, to

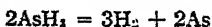
<sup>1</sup> "Kapillarchemie," 2nd Edition, p. 177, Leipzig, 1922

<sup>2</sup> I shall use the term "adsorbate" to indicate the substance adsorbed

<sup>3</sup> Bancroft, *J. Phys. Chem.*, **21**, 734 (1917); "Applied Colloid Chemistry," McGraw-Hill, 1921; "First Annual Report, Committee on Contact Catalysis," *J. Ind. Eng.*

indicate some of the typical cases which show the range of adsorption phenomena involved. Faraday proved that traces of grease destroy the catalytic action of platinum. Mond, Ramsay and Shields showed that mercury behaved similarly. Berliner showed the action of grease on the absorption of hydrogen by palladium. Schönbein pointed out that the hydrides of sulphur, selenium, tellurium, phosphorus, arsenic and antimony cut down the activity of platinum. Maxted has demonstrated the decrease in the adsorption of hydrogen by platinum treated with hydrogen sulphide. Maxted also showed that sulphur, arsenic, lead, zinc, and mercury behaved similarly towards platinum. Henry showed that a reaction product, carbon dioxide, might retard a reaction by reason of its covering up the surface and Fink showed that this was true in the case of sulphur trioxide on platinum in the oxidation of sulphur dioxide. Water vapor inhibits the dehydration of alcohol; hydrogen inhibits the dehydrogenation of alcohol at catalyst surfaces. Water vapor inhibits the catalytic activity at iron-molybdenum surfaces in ammonia synthesis even at 500°C. Oxygen inhibits a variety of reactions at tungsten surfaces at temperatures as high as 2000°K., as the researches of Langmuir have shown. In solutions, the variety of inhibitors of the decomposition of hydrogen peroxide by platinum or enzymic catalysts well illustrates the range of adsorption on such surfaces.

The quantitative study of adsorption by contact catalysts has been neglected. Only recently has systematic investigation been initiated. The results accumulated, however, warrant energetic prosecution of the investigation. Stock, Gomolka and Heynemann<sup>4</sup> made measurements in the course of their investigations on the decomposition of arsine which may indicate some adsorption of arsine on the walls of the containing vessel. Measured pressures of arsine were admitted to glass vessels. The gas was then decomposed by heating. The pressure of residual hydrogen was measured. Since



the hydrogen pressures thus obtained should be exactly  $\frac{3}{2}$

*Chem.* **14**, 326, 444, 545, 642 (1922); Maxted, *J. Chem. Soc.*, **115**, 1050 (1919); **117**, 1280, 1501 (1920); **119**, 225, 1280 (1921)

<sup>4</sup> *Ber.*, **40**, 532 (1907)

the initial arsine pressure. This was not found as the following table of results demonstrates.

Temperature =	15°	25°	35°
$p$ AsH <sub>3</sub> . . . . .	714.2	739.2	764.4 mm.
$p$ H <sub>2</sub> . . . . .	1088.5	1125.9	1163.8 mm.
$\frac{2}{3} p(\text{H}_2) - p(\text{AsH}_3)$ . . . . .	11.5	11.4	11.5 mm.

In the last line is given the difference between the theoretically calculated arsine pressure and that observed initially. Stock and his co-workers ascribed this difference between calculated and observed values to the deviations of arsine from the gas laws. There is a distinct possibility that this deviation is to be ascribed partially to adsorption and partially to the operation of molecular attraction since at the temperatures employed arsine is some 80–100° above its boiling point (–54.8°C.) Stock, Echeandia and Voigt<sup>5</sup> studied these deviations in greater detail. Stock and Bodenstein<sup>6</sup> demonstrated that the reaction velocity measurements on the decomposition of arsine on arsenic surfaces were representable by the equation:

$$-\frac{d(\text{AsH}_3)}{dt} = k(\text{AsH}_3)^{1/n}$$

They explained this as due to a distribution of arsine between gas space and surface in accordance with Freundlich's adsorption isotherm.

$$(\text{AsH}_3)_{\text{adsorbed}} = k_1(\text{AsH}_3)_{\text{gas}}^{1/n}$$

They state, however, that the arsine adsorbed is probably too small to measure. This certainly needs experimental test, and is probably not entirely correct.

Fink<sup>7</sup> measured the adsorption of sulphur trioxide on platinum and showed the existence of an approximately monomolecular layer of this gas on the metal at reaction temperatures usual in the contact process of oleum manufacture. This observation was incorporated in the Bodenstein-Fink theory of gas reactions at catalytic surfaces. The reaction velocity was assumed to be determined by the rate of diffusion of the reactant gases through a film of adsorbed resultant, which film was assumed to vary in thickness with the partial pressure of such resultant.

<sup>5</sup> *Ber.*, **41**, 1309 (1908)

<sup>6</sup> *Ber.*, **40**, 570 (1907)

<sup>7</sup> *Z. physik. Chem.*, **60**, 1 (1907)

As Langmuir has pointed out, with only monomolecular layers possible, this is not satisfactory. Rather, reaction rate is conditioned by the fraction of the surface which is bare of the strongly adsorbed gas ( $\text{SO}_3$ ) under the experimental conditions.

The results of Kuster<sup>8</sup> and Berl<sup>9</sup> are similarly interpretable, the catalysts used being vanadium pentoxide and arsenic pentoxide, the reaction, however, in each case being much slower than with platinum. The researches of L. and P. Wöhler and Plüddemann<sup>10</sup> on the catalytic activity of oxides which might form sulphates as intermediate steps in the process, *e. g.*,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and those in which this is not likely,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , etc., is worthy of study by the student of adsorption in its relation to catalysis. These workers established the undoubted influence of the state of division of the catalyst on its catalytic activity. They showed that gross particle size was not a measure of catalytic action. They attempted to measure effective surface by studying adsorption of acids such as acetic and benzoic acids from solutions by the various catalysts studied. They reached an adverse conclusion in this regard, largely, in the view of the present author, by reason of the specificity of adsorption displayed in the examples studied, a possibility of which the authors were aware but concerning which no large body of available evidence was then to be found.

Langmuir's researches on the clean-up of gases by filaments are too well known to need record here. Those investigations and his studies of catalysis at platinum surfaces<sup>11</sup> have given results from which may be deduced a capacity of such surfaces to adsorb at a maximum a monomolecular film of various gases. Quantitative measurements on platinum, glass and mica confirm this conclusion.

Systematic study of the quantitative data on adsorption by catalysts when subjected to the action of poisons has been carried out by Maxted in recent years.<sup>12</sup> The decrease in activity caused by the poisons lead, mercury, zinc, sulphur and arsenic is directly proportional to the concentration of inhibitor from zero concentration up to that producing practically complete

<sup>8</sup> *Z. anorg. Chem.*, **42**, 453 (1904)

<sup>9</sup> *Ibid.*, **44**, 267 (1905)

<sup>10</sup> *Z. physik. Chem.*, **62**, 641 (1908)

<sup>11</sup> See especially *Trans. Faraday. Soc.*, **17**, 607, 621 (1921)

<sup>12</sup> *Loc. cit.*, p. 97

inactivity. The occlusive power of palladium for hydrogen varies directly as the amount of sulphur present as inhibitor. The amount of lead, as poison, required to reduce the catalytic activity to one-half is very much less than that which reduces the occlusive power to one-half its original value. This may be explained by the fact that, while occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. With metals showing adsorption without marked occlusion there would doubtless be complete identity between loss of adsorptive capacity and loss of catalytic activity.

Systematic studies of adsorption of a variety of gases by metal catalysts for hydrogenation processes and of metals for ammonia decomposition, of oxides for oxidation processes and of a few salts, have been made in the Princeton Laboratories.<sup>13</sup> The measurements have been made over a wide temperature range and in a few typical cases over a range of pressures. In a few cases, the intimate parallelism between adsorptive capacity and catalytic activity has been traced. Pease's recent studies of the hydrogen-ethylene combination and adsorptions on copper, Benton's recent studies of carbon monoxide and hydrogen adsorptions on oxides as accounting for preferential combustion of carbon monoxide in hydrogen are cases in point. Gauger's recent studies of nickel-hydrogen isotherms pave the way to studies of the thermodynamics of such adsorption processes, concerning which practically nothing is now known. Direct measurements of heats of adsorption of gases by catalysts are now being made.

The results so accumulated may now be discussed in detail with particular reference to the aspects of catalysis and adsorption which are involved in such work.

#### ADSORPTION ACCOMPANIES CATALYTIC CHANGE

The general conclusion from the work at Princeton already cited is that adsorption is a condition precedent to catalytic change. The data obtained by Taylor and Burns on hydrogenation catalysts showed marked adsorption of gases which

<sup>13</sup> Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921); Taylor and Burns, *J. Am. Chem. Soc.*, **43**, 1273 (1921); Taylor, *J. Franklin Inst.*, **194**, 1 (1922); Pease and Taylor, *J. Am. Chem. Soc.*, **43**, 2179 (1921); **44**, 1637 (1922), Benton, *J. Am. Chem. Soc.*, **45**, 887, 900 (1923); Gauger and Taylor, *J. Am. Chem. Soc.*, **45**, 920 (1923); Pease, *J. Am. Chem. Soc.*, **45**, 1196 (1923); Dougherty and Taylor, *J. Phys. Chem.*, **27**, 533 (1923); Jones and Taylor, *J. Phys. Chem.*, **27**, 623 (1923)

take part in hydrogenation processes. Low adsorptive capacities were found with relatively inert catalysts. Pease studied this relationship in detail with ethylene and hydrogen on copper showing that high catalytic activity was paralleled by high adsorptive capacity for both gases. Pease further showed that by suppressing the adsorption of hydrogen by partially poisoning the copper catalyst with mercury the catalytic activity was likewise suppressed. Adsorption of both reactants is therefore a condition precedent to efficient catalysis in this case. Benton showed marked adsorption of carbon monoxide, and, to a lesser degree, oxygen by oxide catalysts capable of effecting the combination of these gases. Dougherty and Taylor demonstrated the adsorption of benzene vapors by nickel. Taylor, Benton and Dew<sup>14</sup> have measured ammonia adsorption on a variety of metals which catalyze the decomposition of ammonia. Taylor and Beebe<sup>14</sup> have shown that hydrogen chloride is adsorbed by the copper chloride catalyst of the Deacon chlorine process.

#### THE FORM OF THE CATALYST AND ADSORPTION

The extent of adsorption per unit weight of catalyst is determined by the method of preparation, distribution on inert supports or by subsequent treatment of the surface by catalyst poisons or by heat treatment.

##### ADSORPTIONS ON COPPER

Temperature of reduction of CuO	Nature of CuO	Time required for reduction	Adsorption per 100 g. Cu at 0°C. and 760 mm.		Observers
			H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	
250°C.	Ignited nitrate	Few hours	0.2	2.85	T and Bu
200°C.	Kahlbaum's granules	30-40 hrs.	3.0	8.0	P
150°C.	Kahlbaum's granules	4 days	15.5	..	T and D

##### ADSORPTIONS ON NICKEL

Temperature of reduction of NiO	Nature of NiO	Time required for reduction	Adsorption H <sub>2</sub> per 100 g. at 25°C. and 760 mm.	Observers
300°C.	Ex nitrate	12 hours	47 ccs.	T and Bu
300°C.	Ex nitrate	?	70 ccs.	G and T
300°C.	Ex nitrate	2 days	130 ccs.*	T and Be

\* This catalyst probably more finely divided than the first two

<sup>14</sup> Unpublished work

Variation in adsorptive capacity with variation in the methods of preparation may be illustrated from the work on copper, on nickel and on an oxide such as cupric oxide. These results are strikingly displayed in the accompanying tables.

ADSORPTIONS ON CuO

Nature of CuO	Adsorption per 100 g. Cu at 25°, 760 mm.			Observer
	CO <sub>2</sub>	O <sub>2</sub>	CO	
Strong ignition of Cu	0.015	0.005	0.012	Benton
Calcination of nitrate	0.132	0.00	0.180	Benton
Pptn. of hydroxide	36.2 (0°C.)	1.0 (0°C.)	13.3 (0°C.)	Benton

The effect of a catalyst support on the adsorptive capacity per unit weight of catalyst is well illustrated by the work of Gauger and Taylor with nickel from the calcined nitrate and with nickel spread on a diatomite brick.

H<sub>2</sub> ADSORBED PER G. Ni AT 750 MM.

CATALYST	25°	30.5°	175°	184°	200°	218°	250°
Unsupported Ni.....	0.69	0.63	..	0.53	...	0.48	....
Ni on diatomite.....	....	....	5.2	....	5.1	....	4.73

The best quantitative data on the effect of poisons on catalyst adsorption obtained in the Princeton work are those obtained by Pease on copper. Adsorptions of hydrogen and ethylene on 100 g. Cu were made before and after the catalyst was poisoned with mercury, the quantity of poison being estimated at 200 mg.

ADSORPTION AT 0°C., AND 380 MM.

	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>
Before poisoning.....	3.25 cc.	8.55 cc.
After poisoning.....	0.15 cc.	6.70 cc.

The striking disparity in the influence of the poison on the adsorptive capacities of the two gases is worthy of study. The hydrogen adsorption is reduced to less than 5 per cent. of its initial value. The ethylene adsorption, on the other hand, is still approximately 80 per cent. of its initial value. At the present time, we are inclined, taking these data in conjunction with others on the effect of heat to be presented below, to attribute this phenomenon to differing capacities of surface



atoms to adsorb hydrogen and ethylene. The mercury vapor, on this hypothesis, would be preferentially adsorbed on those portions of the surface which have hydrogen-adsorbing capacity. The effect is probably also due in part to adsorption of ethylene in the pores of the catalyst, which adsorption is not affected by poisons.

Heat treatment of an active catalyst preparation is now our standard method of preparing catalysts with controlled adsorptive capacity or catalytic activity. From a variety of experiments, we may choose the following as indicative of the effect produced by heat treatment.

Catalyst	Heat treatment	Adsorption at 0°C., and 760 mm.		Observer
		H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	
A. Active Cu 100 g.	No heat beyond reduction of oxide at 200°C.	3 70 cc.	8.45 cc.	Pease
B.	A. heated to 450°C. for 1.5 hours	1.15	6.85	Pease
C. Active Ni 27g.	Obtained by reduction of oxide at 300°C.	35	...	Beebe
D.	D. heated at 400°C. for 4 hours	16	...	Beebe

The same abnormal depreciation of the hydrogen adsorption on copper is to be noted here as in the poisoning experiments. This evidence we would interpret thus: A smaller fraction of the surface is capable of adsorbing hydrogen than ethylene. The greater adsorptive force required by surface atoms in order to hold hydrogen is, in our view, to be regarded as possessed by those atoms in the surface which have a greater degree of freedom from the normal crystal lattice of the solid catalyst. These atoms have a lesser fraction of their electron shells surrounded with neighboring copper atoms. They therefore possess a greater surface energy. They would also possess a higher vapor pressure. With the moderate heat treatment accorded to the catalyst in the above mentioned cases these atoms distil to positions of lesser surface energy more readily than do atoms of less freedom in the solid lattice. It is these atoms of high surface energy which will be most affected by heat treatment; they should be the preferred positions of attachment of catalyst poisons.

## THE SPECIFICITY OF CATALYTIC ADSORPTION

Freundlich points out<sup>15</sup> that "since in adsorption by charcoal, the physical characteristics of the adsorbed gas are of far more importance than the specific effect between gas and adsorbent, it is not remarkable that also with adsorption by different adsorbents the influence of the special properties of the adsorbent is strongly suppressed (stark zurucktritt). It can be said with a certain approximation that oftentimes gases are adsorbed, independently of the nature of the adsorbent, in the order of their compressibilities."

This thesis is entirely inapplicable to catalytic adsorption.

The ratio  $\frac{\alpha_1}{\alpha_2}$  for the adsorption of two gases by adsorbents A, B, C, etc., which on the basis of Freundlich's statement would be approximately constant for each adsorbent, A, B, C, etc., may vary quite widely for catalytic adsorbents. The large differences in the ratio of adsorption of carbon monoxide at 0°C. to carbon dioxide at 0°C., obtained by Benton show the specific nature of carbon monoxide adsorption at this temperature for a variety of oxide catalysts.

	Hopcalite	CuO	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>
$\frac{\alpha_{CO}}{\alpha_{CO_2}}$	0.72	0.37	0.22	0.09	0.14	0.08

The same ratio at 25°C. for a few metallic catalysts is obtainable from Burns' measurements.

	Cu	Co	Fe	Pd	Pt Black
$\frac{\alpha_{CO}}{\alpha_{CO_2}}$	10.0	3.6	2.8	288	10.6

It is very evident, since this ratio varies from 0.1 to 300, that the Freundlich relation is entirely untenable for such cases as we are dealing with here. It has only a very circumscribed applicability, namely, to chemically inert adsorbents and easily liquefiable gases. A most striking case of the specific behavior of catalytic nickel is to be found in Freundlich's book (p. 203) in his discussion of some unpublished work by Zisch on the decomposition of nickel carbonyl at nickel surfaces. As Freundlich points out, one might expect, on the basis of the higher critical temperature of nickel carbonyl as compared with

<sup>15</sup> "Kapillarchemie," 2nd Edition, 1922, p. 178

carbon monoxide, a much higher adsorption. Actually, carbon monoxide, even in minute quantities, exerts a powerful retarding action on the decomposition, indicating marked preferential adsorption. Our present knowledge with respect to the structure of nickel carbonyl and its stable configuration on the basis of the Lewis-Langmuir theory of structure immediately suggests the chemical reasons for this specificity of adsorption, unexplainable on the basis of physical characteristics. Other striking variations in ratio of adsorbed gases are to be found in the records of the Princeton work. Consideration of the preceding section on the influence of catalyst poisons and of heat treatment on adsorptive capacity will show furthermore that the ratio of adsorption of gases by a single catalyst is also variable with variation in the method of preparation and of treatment of the catalyst. The rule as to non-specificity of adsorbents must be discarded when cognizance is taken of the data on catalytic adsorbents.

#### SPECIFICITY OF ADSORPTION AND SPECIFICITY OF CATALYTIC ACTIVITY

The influence of specific adsorption in determining specific catalytic activity is best demonstrated by work dealing with the preferential catalytic combustion of carbon monoxide admixed with hydrogen. As is well known, metallic oxides may be used to catalyze the combination of carbon monoxide and oxygen present in equivalent concentrations in a large excess of hydrogen. The mechanism of this preferential oxidation is at once apparent from the adsorption ratio of the two gases at atmospheric pressure on various oxides at  $-79^{\circ}\text{C}.$ , as determined by Benton.

Oxide =	Hopcalite	MnO <sub>2</sub>	CuO	Co <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>
$\frac{\alpha_{\text{CO}}}{\alpha_{\text{H}_2}}$	33	100	34	19	35	17	28

For exact comparison with preferential combustion data adsorptions at low partial pressures of carbon monoxide should be compared with those of hydrogen at approximately atmospheric pressure. The results cited, however, show marked preferential adsorption of carbon monoxide. With metals the preferential nature of the combustion process is less pronounced. With nickel and platinum the hydrogen is freely consumed;

with copper a fair preferential combustion may be attained. Note the following data on adsorption ratios of the two gases at various temperatures and atmospheric pressure and contrast them with the oxide data.

	. Ni	Pt Black	Cu
$\frac{\alpha_{\text{CO}}}{\alpha_{\text{H}_2}}$	0.87 (184°)	3.3 (100°)	12

The data cited are also of interest in connection with the problem of specificity of adsorbent discussed in the preceding section.

#### VARIATION OF ADSORPTION WITH PRESSURE AND THE HEAT OF ADSORPTION

As is well known, the variation of adsorption with pressure on adsorbents such as charcoal is approximately given by the Freundlich equation

$$\alpha = k C^{1/n}$$

where  $\alpha$  = amount adsorbed,  $k$  and  $n$  are constants, the latter being always equal to or greater than unity.

The data on the variation of adsorption with gas pressure with metallic catalysts as adsorbents are few; some of these, however, show striking characteristics. Gauger and Taylor's data on the adsorption isotherms of hydrogen on nickel are the most completely studied thus far. The curves obtained at a variety of temperatures 25–305°C., show the characteristic shape of normal adsorption isotherms so far as absence of discontinuities indicative of compound formation, are concerned; they show, however, this distinction that at a certain pressure at each temperature, a definite saturation capacity of the surface is apparently reached. This saturation capacity is reached at very low partial pressures, 40 mm. at 25°C., and approximately 250 mm. at 305°C. Beyond these pressures, further increase in gas pressure up to atmospheric pressure (*i. e.*,  $\frac{760}{40} =$

19-fold increase in pressure at 25°C.) adds to the amount of gas adsorbed so little as to be within the error of measurement. The same observation is true in the recent results of Pollard,<sup>16</sup> employing hydrogen, and, to a less extent, carbon monoxide on platinum. The amount of adsorbed hydrogen in this case

<sup>16</sup> *J. Phys. Chem.*, **27**, 365 (1923)

does not sensibly increase beyond a gas pressure of 100 mm.

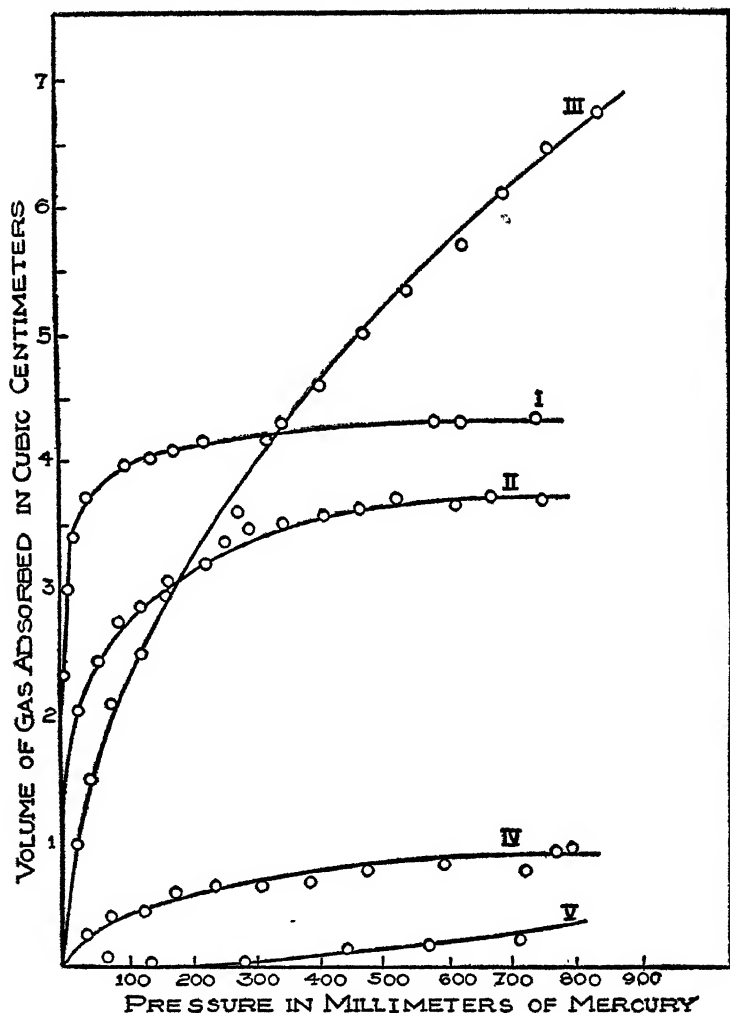


Fig. 1.—Adsorption measurements on copper. Curve I, Carbon monoxide at 0°; Curve II, Carbon monoxide at 80°; Curve III, Carbon dioxide at 0°; Curve IV, Carbon dioxide at 80°; Curve V, Carbon monoxide measured at 80° over sample used in reaction velocity measurements.

Pease's data on the adsorption of hydrogen by copper show a similar if less pronounced attainment of saturation capacity.

The adsorption of hydrogen at 380 mm. pressure was 90 per cent. of that at atmospheric pressure. Similar behavior with respect to carbon monoxide on copper is shown in the accompanying Fig. 1 which represents some measurements of Jones and Taylor on the adsorption isotherms of carbon monoxide and carbon dioxide on copper at 0°C. and 80°C. Earlier work on adsorbents of the charcoal type has not indicated the attainment of saturation capacity of the surface even at pressures well beyond atmospheric pressure. A further distinction is also noticeable. Gauger and Taylor's results show that the adsorptive capacity of hydrogen on nickel at saturation is, at 305°C., as much as 60 per cent. of the saturation capacity at 25°C. Some recent data obtained by Dew on copper show adsorptions of hydrogen in the ratio of 10 to 8.7 at 0° and 110°C. and atmospheric pressure. Contrast this with the data concerning adsorption on charcoal. The adsorption of carbon monoxide at 400 mm. and 46°C. is only 8 per cent. of that at -78°C., this temperature interval being about the same as that obtaining in Dew's case and less than one-half of that recorded above with nickel and hydrogen. The adsorption of carbon dioxide on charcoal at 150°C. and atmospheric pressure is less than 7 per cent. of that at -78°C. These striking differences both in the pressures at which saturation is attained and in the variation of adsorption with temperature are undoubtedly of fundamental importance in the study of catalytic adsorbents.

Data on adsorption isotherms may be utilized to evaluate the heat of adsorption of gases on the adsorbent surface. Gauger and Taylor using the minimum pressures at which saturation is reached at the several temperatures, and substituting these in the equation

$$\lambda = 4.57 \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1}$$

obtained a value for  $\lambda$  the heat of adsorption of 2500 calories. This calculation is in error since the equation should be applied (see Freundlich, 2nd Edition, p. 182) to the pressures of  $P_1$  and  $P_2$  at which *equal* amounts of gas are adsorbed. The data of Gauger and Taylor do not lend themselves readily to such computations if accuracy is desired, as the pressures at which equal weights of gas are adsorbed at different temperatures are small and consequently most liable to error. From the best

available data, however, calculated in the correct manner, a value for the isosteric heat of adsorption of  $15,000 \pm 3000$  calories was obtained.

In the meantime, a direct determination of the heat of adsorption of hydrogen on nickel has been carried out by Beebe and Taylor. We shall report elsewhere the details of these measurements. It will suffice here to say that, on a freshly prepared, highly active, sample of nickel, a heat of adsorption equal to 13,500 calories per mol was obtained. It is to the magnitude of this value we wish to draw special attention.

It is at once evident that there is a wide deviation in this case between the heat of adsorption and the heat of liquefaction of hydrogen which latter cannot be much greater than 450 calories per mol. Further, a little consideration will show that it is to this abnormally high heat of reaction that the characteristic curves of the nickel-hydrogen isotherms are to be attributed. From the isotherms it may be shown that with a given sample of nickel 8.7 cc. of hydrogen were adsorbed at  $25^\circ\text{C}$ . and 40 mm. pressure. Utilizing the directly observed value for  $\lambda = 13,500$  calories, we may now calculate at what pressure 8.7 cc. of hydrogen will be adsorbed at any other temperature. Thus, for  $T = 184^\circ\text{C}$ ., we have

$$13,500 = \frac{4.57 \times 298 \times 457}{(457-298)} \log \frac{P_2}{40}$$

whence  $P_2 = 71,300$  mm. approximately; or, somewhat less than 100 atmospheres is the pressure at which the nickel surface will be covered with 8.7 cc. of hydrogen gas at  $184^\circ\text{C}$ . But, Gauger's measurements show that already at 150 mm. pressure 8 cc. of gas are adsorbed. A further 100 atmospheres therefore only produce an additional adsorption of 0.7 cc., a result in entire agreement with that found experimentally, namely, that within the range 150-760 mm. at  $184^\circ\text{C}$ ., and in the range 40-760 mm. at  $25^\circ\text{C}$ ., the adsorption was, within the error of measurement, constant. In a similar manner, it may be calculated that at  $305^\circ\text{C}$ . it would require some 2,540,000 mm., some 3000 atmospheres gas pressure to cover the surface with 8.7 cc. adsorbed gas. In other words, it is to the abnormally high heat of adsorption that the observed independence of adsorption with pressure is to be attributed. In con-

firmation of this observation, it is interesting to note that Mond, Ramsay and Shields' measurements of the heat of adsorption on platinum of hydrogen gave a value of 13,760 calories per mol of adsorbed gas. Langmuir estimates the heat of adsorption of carbon monoxide on platinum at 30,000 calories. These high values are consonant with the shape of Pollard's curves for the adsorption of these gases on platinum. The data of Jones and Taylor on carbon monoxide are suggestive of the same high value for heat of adsorption. A calculation from two pairs of isosteres gives a value of 6500 calories  $\pm$  300 calories. This is markedly higher than the value for the heat of liquefaction, which, on the basis of Trouton's rule,  $\lambda = 22T_B$ , should be  $22 \times 81 = 1780$  calories. It is interesting to note that from Pease's data on ethylene, a gas whose isotherm at 0°C. is much more reminiscent of isotherms on charcoal the value deduced from the isosteres at 0°C. and 20°C. (480 mm. and 760 mm.; 5.5 cc. adsorbed) for the heat of adsorption may be calculated to be 3750 calories which is exactly what would be deduced from Trouton's rule for heat of vaporization. From the isosteres at lower pressures higher heats of adsorption are calculable. From the isostere for 0.85 cc. (200 and 380 mm. approximately) the calculated value is about 5100 calories.

It is evident, therefore, that, in the investigation, on the one hand, of adsorption isotherms of various catalyst-gas systems and, on the other hand, in the direct determination of heats of adsorption, we have two powerful instruments with which to examine further into the mechanism of catalytic action. Both of these instruments are being intensively employed.

We regard the slight variation of adsorption with pressure after the initial strong adsorption at the lower partial pressures in several of the cases studied as the strongest evidence in favor of Langmuir's theory of a monomolecular layer. There is evident little or no tendency to build up layers of adsorbed molecules on such surfaces. Indeed, the results at the higher temperatures suggest that considerable pressures may be necessary before even the surface is covered with a layer one molecule deep. With ethylene and ethane at 0°C., in Pease's experiments and with carbon dioxide at 0° in Jones and Taylor's experiments with copper, there is possible evidence of lique-



faction phenomena in addition to the specific adsorption of gas-solid.

It is interesting to obtain evidence of this from another direction in which the difficulties associated with the definition of the surface are absent. This is so in a recent publication by Iredale<sup>17</sup> who has investigated the adsorption of methyl acetate on liquid mercury by determining the change of surface tension of mercury with varying partial pressures of the vapor. The following table shows this variation from zero pressure to 227 mm., the saturation pressure at the temperature employed (26°C.).

V. P.....	0	19	62	109	137	157	227 mm.
$\gamma$ .....	472	444	423	419	418	417	412-370 dynes/sq. cm.

It will be noted that from 62 mm. up to the saturation pressure, there is only a slight variation in surface tension with change in vapor pressure. This points to the attainment of an approximately monomolecular adsorbed layer at less than one-third of the saturated vapor pressure. Iredale has calculated the amount adsorbed at 62 mm. as of the order of  $4.5 \times 10^{-8}$  g. of methyl acetate per sq. cm. mercury. This is equivalent to  $0.37 \times 10^{15}$  molecules per sq. cm. or to an area of approximately  $27 \times 10^{-16}$  sq. cm. per molecule which is comparable with that deduced by Langmuir for the area occupied by such esters when oriented at a water surface.

#### ADSORPTION AND CATALYTIC ACTIVITY

This abundance of evidence as to the existence of adsorption with catalytic materials must not, however, be taken to imply that the existence of adsorption is the sole criterion of catalytic change. On the contrary, abundant evidence is forthcoming that adsorptive capacity is no sufficient criterion of catalytic

Reaction	Catalysts	Non-catalysts
$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$	Ni, Co, Fe, Pd	Cu, Pt
$2\text{CO} = \text{CO}_2 + \text{C}$	Ni, Co, Fe	Cu, Pt
$\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$	Ni	Cu

efficiency. The poor catalytic properties of charcoal and silica gel constitute one such piece of evidence. Furthermore, the specificity of catalysts, even when adsorptive capacity for re-

<sup>17</sup> *Phil. Mag.*, **45**, 1088 (1923)

actants and resultants is demonstrated, is yet another line of evidence. All of the metals listed in the subjoined table show measurable adsorptions of the reacting gases in the reactions indicated. They display, however, the marked divergencies which are noted in the table.

I have elsewhere suggested that orientation of the adsorbed molecules may account in part for such specificity. It seems possible to picture the second reaction occurring if the metal-gas linkage be Me-CO in the catalytic reactions and Me-OC in the non-catalyzed reactions. And as yet there seems to be no evidence either way in this regard.

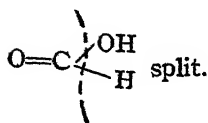
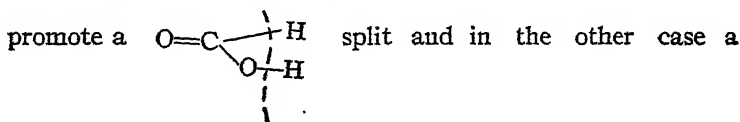
While, however, it is certain that orientation may in some cases be called in to assist in the explanation of mechanism, it is equally certain that orientation in adsorption is not sufficient to account for all such specificity of catalytic action. It will be generally agreed that such organic molecules as formic acid or the esters will be adsorbed to the catalyst at the  $\text{—C=O}$  grouping. And yet, as the researches of Adkins have effectively demonstrated, it is possible to alter, almost at will, the nature of the decomposition produced in a body so adsorbed by suitable alteration of the catalyst employed.

The conclusion seems inevitable that the cause of specificity lies in the disturbance exercised by the process of adsorption on the configuration of the adsorbed molecule. We have seen already that there are evidences of profound change in the abnormally high thermal magnitudes associated with certain typical activating adsorptions. The adsorption of hydrogen by nickel, as the heat of adsorption reveals, is no such small disturbance of the electronic forces of the molecule as is involved in a simple condensation process. The disturbance caused is more deep-seated. When no such deep-seated disturbance of the molecule occurs, as in the case of adsorption by charcoal and silica gel, values more closely approximating heat of condensation obtaining, little catalytic activity is manifest.

We look therefore towards an explanation of catalysis in the influence exercised by the adsorbent on the configuration of the adsorbate. By the adsorption, the whole electron field of the adsorbed molecule must be altered. The extent of this alteration must be revealed in part in the measurement of the energy changes involved. The actual alteration achieved

must be determined by the nature of the adsorbent. We can exemplify this in the comparatively simple case of the decomposition of ammonia at metal surfaces where variation in the nature of the decomposition and in the ease of decomposition is determined by the nature of the metal constituting the surface. At a sodium surface sodamide is formed and hydrogen set free. At copper surfaces ammonia is freely adsorbed but with difficulty dissociated. With nickel, and still more so with iron and with iron-molybdenum, dissociation into elementary constituents occurs. Undoubtedly, the interplay of electrons as a result of the adsorption association is responsible for the divergencies.

In the more complex cases of the organic molecules the nature of the decomposition products must be determined by the nature of the changes in configuration caused by the attachment. That such attachments are capable of effecting a pronounced change throughout the molecule is well known to all chemists in a somewhat different guise. The introduction of a chlorine into the final methyl group of all the fatty acids exercises an influence on the molecule which is transmitted throughout the length of the hydrocarbon chain and is revealed in the extent of dissociation of the acid. Thus, the acidic hydrogen of chloracetic acid is much less firmly attached to the anion than is the hydrogen ion in acetic acid, as is revealed by its pronouncedly greater degree of dissociation. The same is true with propionic, butyric and the higher acids. On the other hand, the substitution of an  $\text{—NH}_2$  grouping for  $\text{—Cl}$  has the opposite effect. It does not seem unreasonable, therefore, to postulate that the nature of the catalyst should exercise an influence on the adsorbate which is transmitted throughout the length of the adsorbed molecule; so that, in the one case, for example with formic acid, the nature of the linkage should



Progress in such directions, steadily achieved, proceeding from the simple to the more complex, will surely bring us to the desired goal.

DISCUSSION ON H. S. TAYLOR'S PAPER

THE PROBLEM OF ADSORPTION FROM THE STAND-  
POINT OF CATALYSIS

C. A. SHULL: I would like to ask Dr. Taylor whether he is willing to express his opinion in regard to the problem of chemical union in adsorption.

H. S. TAYLOR: I can express an opinion but I do not know whether it will be worth anything. The influence exercised by the introduction of chlorine substituents into the acetic acid molecule is very well known. Chlorine so introduced entirely alters the acidic behavior of the acid. Acetic acid is a very weak acid. Chloroacetic acid is a stronger acid. It is therefore evident that by introducing chlorine at one end of the molecule you alter the properties of the hydrogen atom at the other end of the molecule. Now this is true generally of the introduction of halogens into fatty acids no matter how long the hydrocarbon chain. I believe that the attachment of organic molecules to a catalytic agent by adsorption processes such as we have discussed effects a similar influence on the properties of the molecule adsorbed. It would seem that, depending on the nature of the material to which the adsorbate is attached, the electronic configuration of the whole molecule attached may be rearranged, in different manners on different contact agents, tending to give different products as a result of such catalytic adsorption.

C. A. SHULL: Dr. Taylor has called attention to the fact that charcoal is not very catalytic in its activity. I wish to call attention to a paper by Barber, published last year, in which he argues for the adsorption nature of the processes of respiration. He used charcoal as one of his examples and proved that charcoal does have some catalytic activity. Also we have estimated a very high adsorption capacity in plant substance: the adsorption of water by starch for instance. As I recall, the estimates were based on a study of the heat properties some sixty years ago when absolutely dry starch was treated

with water, and on the basis of that it was estimated that the pressure was something like 13,000 atmospheres. Of course starch has no catalytic activities so far as I know, but it seems in substances of a certain nature we do have very high adsorption values.

H. S. TAYLOR: It is well known that, although the catalytic activity of charcoal is low, it does have a definite catalytic oxidation activity.

R. E. WILSON: Dr. Taylor gave us some very interesting data with regard to the temperature of reduction of the oxide and on the amount which it would adsorb, showing that 150° reduction is much more effective than 200°. It seems rather surprising, however, that such low temperature should have any direct effect in itself on the structure of a thing like metal. Furthermore, the observations which he made on the effect of having the stuff distributed would seem to me to indicate that the real difference was not the temperature but the rate at which the reaction of reduction proceeded. It probably made a temperature several degrees higher. It would seem that the distribution would tend to prevent that rise from being so large. I would like to have Dr. Taylor's opinion on that. One other question: I would like to ask as to the diagram on the board. Getting the heat of adsorption by calculations based on an equal amount of surface covered, Dr. Taylor has made the implied assumption that equal amounts of surface will be covered by an equal number of molecules at those two different temperatures. Now, the coefficient of expansion of the gas is rather large, and might it not be that those two different lines may merely represent the same amount of surface covered?

H. S. TAYLOR: Yes, I suppose that eventually one has to take into account the variation of the superficial area occupied by a molecule when it "sits down." The copper and the nickel at the same time expand, and I suppose we have got to take that into account too. The first improvement on that particular calculation would be to make a correction for the expansion of the adsorbent and then to make a few calculations as to what the extent of the change due to adsorbate would be. I have only learned in the last two or three weeks how to make the calculation at all correctly, so you must forgive me on that score.

With regard to the question of overheating which causes the very great derangements, I am inclined to think that that plays a very considerable part, because everyone knows that the easiest way to destroy a catalytic agent is to reduce it so rapidly that the material gets very hot, and then adsorption capacity and catalytic activity likewise disappear. On the other hand, the influence of temperature is undoubtedly a quite important factor in spite of the fact that the catalyst has had such low temperature treatment as compared with the normal temperatures at which metals distil. Now I believe that that indicates that a certain portion of the surface is in an extremely active condition, and that for example, it is that fraction of the surface which adsorbs the reacting substance. Suppose one considered a plane surface of copper, and that coming up from the normal surface of the copper we find partially attached copper atoms, then the vapor pressure of these copper atoms is going to differ undoubtedly from that of the copper atoms in the surface. They will distil at very much lower temperatures. I am inclined to believe that the atoms partially attached to the surface have a high adsorption capacity, and that heat treatment causes them to distil over into positions of a lesser external free energy, causing a remarkable drop in the adsorption capacity. The same may hold also in poisoning. What happened to the copper on the introduction of mercury? In my opinion, the mercury attached itself to the active copper atoms and left the remaining copper atoms entirely alone. I am quite aware that that isn't the only possible explanation. It may be that the mercury covers the whole surface and that we are then measuring adsorption on mercury.

R. E. WILSON: Can you measure the quantity of mercury that is adsorbed?

H. S. TAYLOR: Yes, we actually know the quantity of mercury that is adsorbed.

J. ALEXANDER: Has anybody ever made any X-ray examination of catalysts of that character? It would seem that one factor influencing the activity is the amount of free surface of the catalyst, and of course the more highly crystalline that free surface of the catalyst, the less surface would be exposed for catalytic work. I do not doubt but that a temperature of  $300^{\circ}$  would have a very marked effect on copper.

H. S. TAYLOR: The General Electric Company has very kindly investigated some of our catalytic agents by the X-ray, and they have found in every sample that we have submitted to them identically the same X-ray result as the massive crystal gives. We have submitted to them catalysts which have been prepared by as low temperature reduction of oxides as we could obtain, and we have submitted to them oxides which have been prepared from precipitated hydroxides and in every case they reported to us the same crystallinity as would be present in normal crystalline materials.

J. ALEXANDER: Of course, the crystallinity would naturally be the same, but if there were no random groups, then the whole thing would seem to depend upon the dispersion of the crystals.

H. S. TAYLOR: Yes, undoubtedly. If you reduce copper oxide at  $150^{\circ}$  you get a substance which anybody would say was not copper. It has a dirty brown color which one might think was due to a lower oxide. If you reduce at  $150^{\circ}$  and then heat in hydrogen to  $450^{\circ}$ , you will get at least a 10% shrinkage in volume; the copper will change from a dirty brown copper to a bright pink copper.

E. O. KRAEMER: I should like to ask Dr. Taylor whether the character of the lines varied in the case of the X-ray spectrum with the method of the preparation of the catalyst.

H. S. TAYLOR: I have no figures at all with regard to the breadth of the lines.

E. O. KRAEMER: That would be the significant feature, I should think, would it not?

H. S. TAYLOR: Yes, no doubt.

F. DANIELS: In regard to the adsorption of phosphine, an experiment of Trautz and Bhandarkar (*Z. anorg. allgem. Chem.*, 106, 95 (1919)) is interesting. It was found that the decomposition of phosphine is catalyzed by the walls of the containing vessel, and this fact must show that phosphine is adsorbed; for heterogeneous catalysis implies adsorption, although adsorption does not necessarily carry with it catalysis.

In regard to the difference in the rate of reduction on supporting material, I would like to ask Dr. Taylor if an explanation on the basis of auto-catalysis by metallic nickel is not satisfactory. If the reaction spreads from points of metallic nickel,

the reaction should go slower when the nickel oxide is distributed as small islands on a supporting medium, for the catalytic reaction cannot spread from one island to the next.

H. S. TAYLOR: That is actually true, nickel oxide is an inter-phase reduction, and it was suggested in a paper by Dr. Gauger that you had localized islands so that the auto-catalytic activity did not affect the whole mass but only the islands.

L. H. REYERSON: It might be of interest to mention, in connection with Prof. Taylor's paper, some results that we have obtained by preparing catalysts at very low temperatures. Metals were reduced from solutions of their salts by hydrogen adsorbed in silica gel at about  $-20^{\circ}\text{C}$ . These metals formed a black deposit upon the gel and in the case of palladium, platinum and copper marked reductions of ethylene to ethane have been observed at room temperature. In fact in some cases at zero degrees we have obtained as much as 90% conversion of ethylene.



[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN]

## MEMBRANE POTENTIALS AND THEIR RELATION TO ANOMALOUS OSMOSE

By F. E. BARTELL

The phenomenon of osmose of liquids through membranes with the attendant osmotic pressure is well known. As a generalization, the statement is usually made that, when we have a solution separated from its solvent by a semipermeable membrane, there will result a flow of liquid through the membrane from solvent or dilute solution to the more concentrated solution. In recent years we have found numerous exceptions to this rule. We have found cases in which flow of liquid through a membrane is from concentrated to dilute solution. This process we have termed negative osmose. Some of the best examples of negative osmose are to be found in connection with life processes, in fact, negative osmose plays a most important part in the existence and growth of both animal and vegetable organisms.

It is readily appreciated by the biologist that the passage of fluid through many of the membranes, of which the essential body organs are formed, may be accounted for by osmotic pressure effects. On the other hand, normal osmotic effects do not account for the direction of flow of liquid through other membranes within the same body. The flow of liquid through portions of the intestinal walls, as also secretion by the kidneys, is found to be in a direction just opposite that demanded by normal osmose. The same is true of different organs in disease.

Although much work has been done on this problem, no satisfactory explanation for this phenomenon has been forthcoming. In order to present some kind of "explanation," these effects have often been referred to as the "vital attributes" of the system in question.

When we have a system in which a perfectly semi-permeable membrane separates a solution from its solvent, the general gas law  $PV = nRT$  should apply provided we substitute  $\pi$  osmotic pressure for  $P$  gaseous pressure. Accordingly, the magnitude of osmotic effects should vary directly with the concentration.

The above generalization will hold only when the membrane is strictly semi-permeable. It is considered by Tinker<sup>1</sup> that a membrane is of this type only in case it is wetted by the solvent and in case no solute is adsorbed by the membrane. Similar views have been expressed by Bancroft.<sup>2</sup> A copper ferrocyanide membrane with sugar solution answers this requirement.

The writer has shown<sup>3</sup> that distinct osmotic effects can be obtained with modified copper ferrocyanide membranes and sugar solutions when the pore diameters of the membrane (*i. e.*, 200 pores in an area 1.54 sq. cm.) are as large as approximately one micron. With pores larger than this the "leak" became so great that definite pressures could not be measured. In recent work with collodion membranes osmotic effects have been obtained with membranes having pore diameters of 1.6 microns.<sup>4</sup>

Positive osmotic effects have been obtained with membranes rigid and apparently inert chemically, such for example as carbon<sup>5</sup> and unglazed porcelain.<sup>6</sup> When sugar solutions were used with porcelain membranes it was found that the rate of osmose increased directly with increase in concentration of solution. Solutions of  $\text{FeCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$ , etc., gave an abnormally rapid osmose while solutions of  $\text{LiCl}$ ,  $\text{LiNO}_3$ ,  $\text{MgCl}_2$ ,  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , etc., gave a decidedly negative osmose, that is, the direction of flow of liquid was from concentrated to dilute solution. These negative effects were obtained with membranes having pore diameters slightly less than 0.4 micron. In somewhat later work Bartell and Hocker<sup>7</sup> using porcelain membranes of approximately the same porosity as the above obtained rather surprising anomalous effects, for example, with a dilute solution of  $\text{HCl}$ , 0.005 *N*, the osmose was positive, then with a somewhat higher concentration 0.01 *N* the osmose was less positive, while at a still higher concentration the osmose again became increasingly positive. These relationships are shown by the curve in Fig. 1, in which osmose values are plotted against

<sup>1</sup> *Proc. Roy. Soc.*, **92A**, 357 (1916); **93A**, 268 (1917)

<sup>2</sup> Bancroft, *J. Phys. Chem.*, **21**, 441 (1917)

<sup>3</sup> *J. Phys. Chem.*, **16**, 318 (1912)

<sup>4</sup> Bartell and Carpenter, *J. Phys. Chem.*, **27**, 252 (1923)

<sup>5</sup> Bigelow and Robinson, *J. Phys. Chem.*, **22**, 1153 (1918)

<sup>6</sup> Bartell, *J. Am. Chem. Soc.*, **36**, 646 (1914)

<sup>7</sup> *J. Am. Chem. Soc.*, **38**, 1036 (1916)

concentration of solution. The curve is N shape and this type of osmotic effect we have termed anomalous osmose.

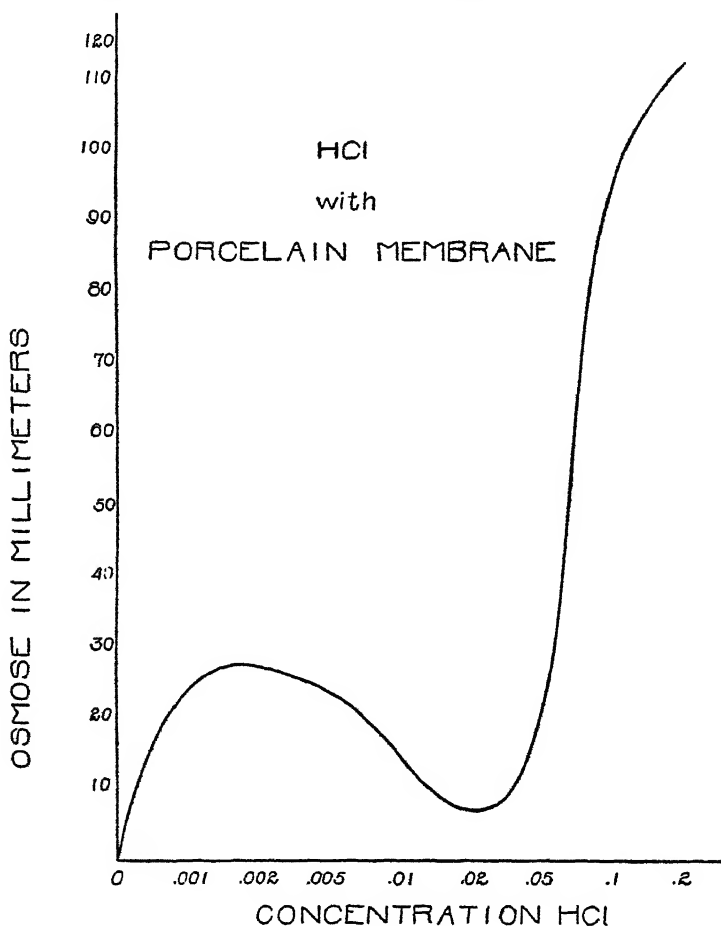


Fig. 1.

#### ANOMALOUS OSMOSE

We have found that anomalous osmotic effects may be obtained with a variety of membranes, such as collodion<sup>8</sup> (organic composition) unglazed porcelain<sup>9</sup> (inorganic composition),

<sup>8</sup> Bartell and Carpenter, *J. Phys. Chem.*, **27**, 101, 252, 347 (1923)

<sup>9</sup> Bartell and Hocker, *loc. cit.*

gold beaters skin and calves bladder<sup>10</sup> (animal membranes), and parchment paper<sup>11</sup> (vegetable membrane).

Anomalous osmotic effects are believed to be caused primarily by the operation of electrical forces which forces are due to electrolytes present in the solution. It is assumed that as a result of electrolytic dissociation there exists an electrical orientation within the system which functions in a manner similar to that in the well-known electrical osmose. One set of electrical forces are so oriented that they may be considered to operate between the two faces of the membrane and for designation the resulting potential will, in this paper, be termed the membrane potential.

The second set of electrical forces are operative along the pore walls of the membrane in the form of an electrical double layer and will be termed the capillary potential.

It seems probable that one of the most important requirements for the appearance of anomalous or negative osmotic effects is the precise diameter of the membrane pore.<sup>12</sup> A change in the shape of the osmose curve may be effected by a change in pore diameter; for example, a collodion membrane with pore diameter of 0.7 micron with a 0.001 *M* solution of  $K_3FeC_6N_6$  gave at the end of two hours an osmose of 32.0 mm. with a 0.01 solution under similar conditions the osmose was 94.5. The magnitude of osmose increased with increase of concentration as it should.

On the other hand a collodion membrane with pore diameter of 1.6 microns gave with a 0.001 *M* solution an osmose of 88.5

TABLE I

Pore diameter of membrane in microns	Conc. of $K_3FeC_6N_6$	Osmose in mm.
0.7	0.001	32.0
0.7	0.01	94.5
1.6	0.001	88.5
1.6	0.01	44.0

mm. and with a 0.01 *M* solution gave 44.0 mm. This membrane with the larger pores behaved quite unlike the other mem-

<sup>10</sup> Bartell and Madison, *J. Phys. Chem.*, **24**, 444, 593 (1920)

<sup>11</sup> Bartell and Sims, *J. Am. Chem. Soc.*, **44**, 284 (1922)

<sup>12</sup> Bartell and Carpenter, *J. Phys. Chem.*, **27**, 252 (1923)

brane. In this case an increase in concentration resulted in a decrease in osmose value. These relationships are shown in Table I and in Fig. 2.

From the above it appears that the osmotic flow of a given solution through a membrane may be caused to change its di-

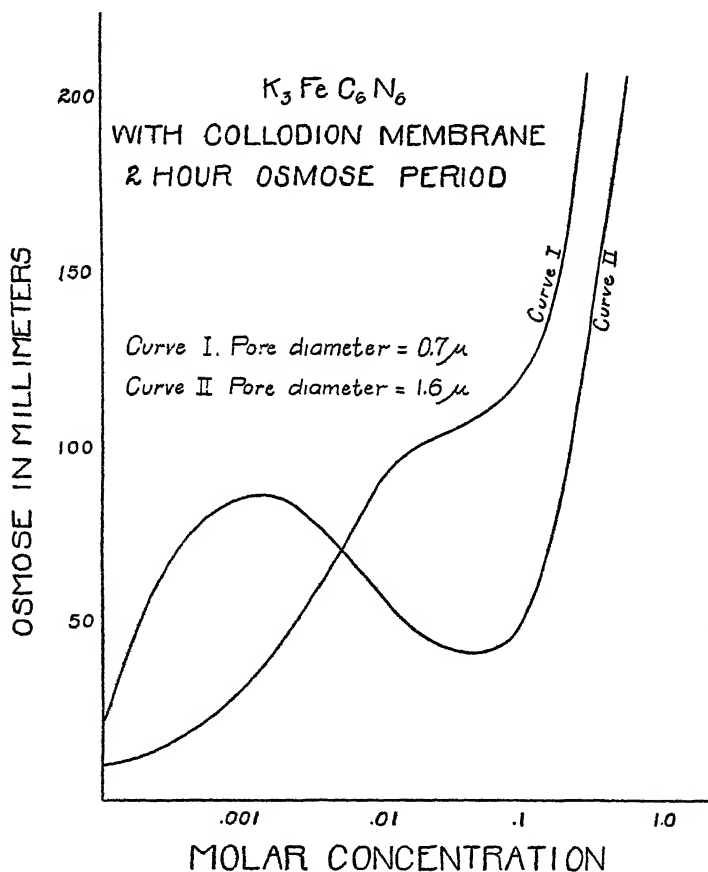


Fig. 2.

rection by a comparatively slight change of pore diameter of the membrane.

#### ELECTRICAL OSMOSE

In electrical osmose two compartments of a cell are separated

by a slightly permeable membrane. (Fig. 3) The cell is filled with liquid, preferably with a very dilute solution of a substance capable of dissociating electrolytically. An electrode is placed in each compartment and an electrical current is caused to flow through the cell. In case the membrane is electro negative to the solution there will result a flow of liquid through the membrane to the negative electrode (cathode). A

## ELECTRICAL OSMOSE

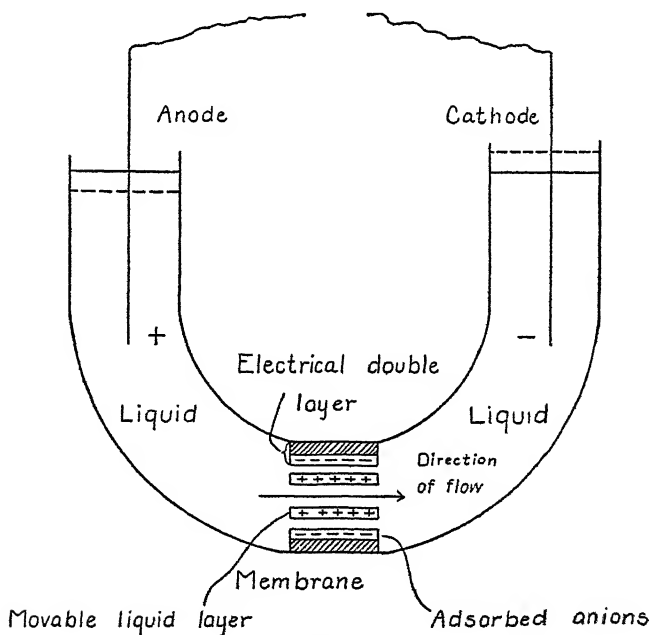


Fig. 3.

review of this phenomenon has been amply covered by Briggs.<sup>13</sup> It is to be noted that the direction of flow of liquid is dependent upon (1) the orientation of the electrical force impressed upon the system and (2) the orientation of the electrical signs existing between the membrane pore walls and the liquid within the pores.

<sup>13</sup> *J. Phys. Chem.*, **21**, 198 (1918); Second Report on Colloid Chem., Brit. Assoc. Adv. Sci. 1918

Freundlich<sup>14</sup> has developed the following expression for the quantity of liquid electrically transported in unit time through a membrane of given area.

$$V = \frac{q\epsilon ED}{4\pi\eta l}$$

$V$  represents the amount of liquid transported through a membrane of cross sectional area  $q$  when the fall in potential through the capillary of length  $l$  is equal to  $E$ .  $\epsilon$  represents the potential of the Quincke-Helmholtz electrical double layer at the solid liquid interface.  $D$  is the dielectric constant of the liquid and  $\eta$  its viscosity.

From this expression it follows that the transport of liquid

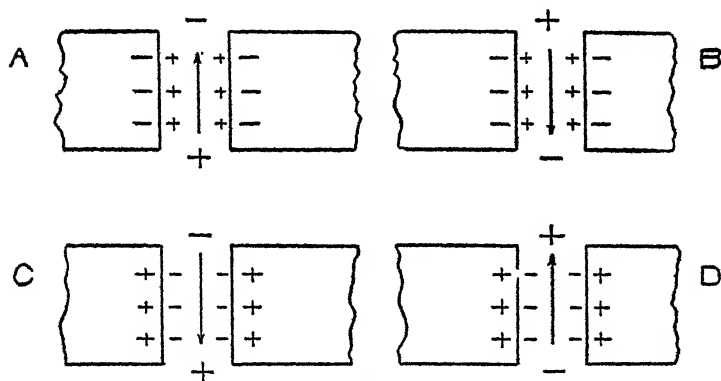


Fig. 4.

$V$  through a given membrane is directly proportional to the two electrical potentials of the system,  $E$  and  $\epsilon$ .

#### EVIDENCES OF RELATIONSHIP BETWEEN ANOMALOUS OSMOSE AND ELECTRICAL OSMOSE

During numerous investigations of recent years, Girard,<sup>15</sup> Loeb,<sup>16</sup> Bartell and co-workers,<sup>17</sup> and others have found that the direction of flow of liquid through a membrane, during anomalous osmose is closely related to the electrical orientation

<sup>14</sup> Freundlich, "Kapillarchemie," 1909, 225

<sup>15</sup> *Compt. rend.*, 146, 927 (1908); 148, 1047, 1186 (1909); 157, 99 (1910); 159, 376 (1914)

<sup>16</sup> "Colloid Chem. of Proteins," 1922, and numerous papers

<sup>17</sup> *Loc. cit.*

of the cell system. The precise cause of the electrical orientation and the precise operation of the electrical forces necessary to bring about given osmotic effects have received somewhat different explanations from the various investigators. Up to the present time no comprehensive explanation has been offered which has been generally accepted.

It is accepted that four different conditions of electrical orientation may exist. (Fig. 4)

It would seem that with electrical orientations as in *A* and *D* (the concentrated solution is represented as being above the membrane) abnormally positive osmose would result, while with conditions as in *B* and *C* abnormally low or even negative osmose would result.

That the above conforms to results of experiment is shown by the following curves.

The curves in Fig. 5 represent osmotic effects obtained with

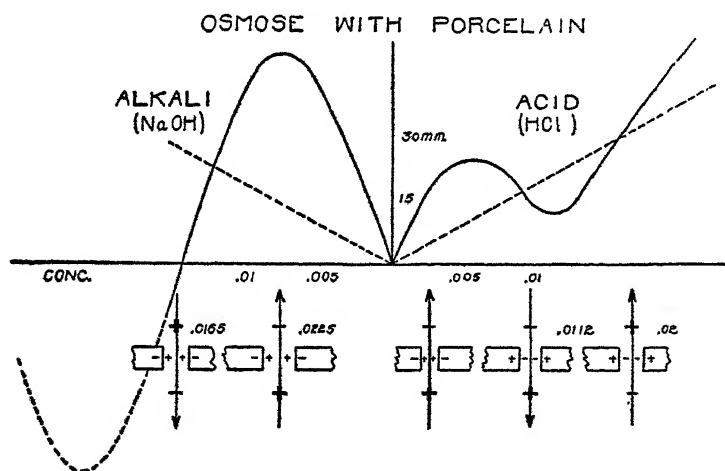


Fig. 5.

porcelain membranes. On the right is given the osmose-concentration curve for HCl and on the left the osmose-concentration curve for NaOH. Below the curves, in position corresponding to the concentration, is represented diagrammatically the electrical orientation of the cell system (the numbers represent membrane potentials in volts). It is noted that



in every case the type of osmose is as is demanded by the electrical orientation of the cell system.

Curves in Fig. 6 are similar curves for gold beater's skin membranes. The osmose curves in this case are of the same general type as the curves for the porcelain membrane. Here also the direction of osmose is as is demanded by the electrical orientation of the system.

#### THEORY OF ANOMALOUS OSMOTIC EFFECTS

1. It is assumed that in all osmotic systems (systems consisting of two liquids of different concentrations separated by a permeable membrane) there will exist a tendency for normal osmose, *i. e.*, a tendency for flow of liquid from dilute to concentration solution. It is further assumed that a superimposed

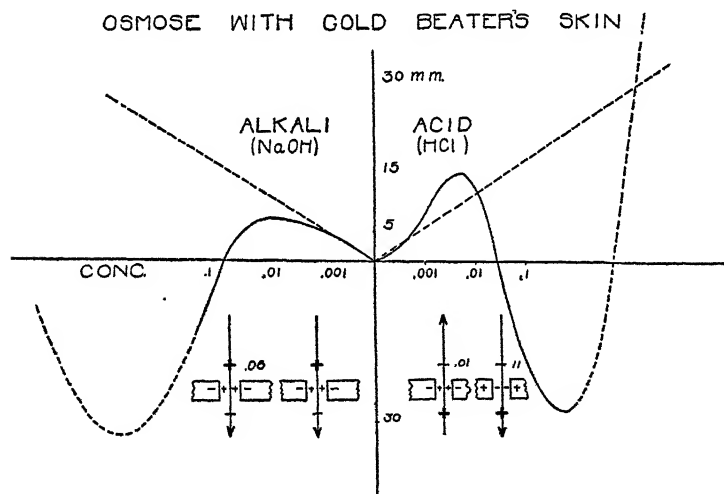


Fig. 6.

tendency due to electrical effects may be simultaneously present, that this force may work in the same direction with normal osmose giving thereby abnormally positive osmose or that it may work in opposition to the normal osmotic force giving abnormally low or even negative osmose.

2. It is assumed that the electrical orientation of the membrane system is due to diffusion of electrolyte through the membrane, the difference in the migration velocities of the

ions determining the electrical sign. This potential tends to function as does the potential represented by  $E$  of the above equation.

3. It is assumed that an electrical double layer is formed along the pore wall due to selective adsorption of cations or anions. The resulting potential corresponds to  $\epsilon$  in Freundlich's equation.

4. We assume the existence of an electrical circuit which makes possible a continuous flow of electrical energy from one compartment of the cell to the other during the flow of liquid through the connecting capillaries, the "return circuit" taking place through the medium of the electrical double layer.

We shall now consider in more detail than has been done in our previous papers the following points:

1. The formation of *membrane potential*, *i. e.*, potential existing between the two faces of the membrane.

2. The formation of *capillary potential*, *i. e.*, potential on pore wall.

3. The conducting medium between the two compartments of cell, *i. e.*, the electrical circuit making possible a continuous flow of electrical energy from one cell to the other during the flow of liquid through the capillaries.

#### MEMBRANE POTENTIAL

The difference of potential which is noted between the two compartments of an osmotic cell separated by a porous membrane may be considered to be the difference of potential operating between the two faces of the membrane. This potential we have measured and have reported in previous papers. It seems most reasonable to believe that this potential is the result of diffusion of electrolyte through the pores of the membrane and is set up by the unequal velocities of migration of the ions passing through the membrane.

Were this diffusion unhindered by external forces, the resulting potential could be expressed by the well-known Nernst formula.<sup>18</sup>

For an electrolyte with univalent ions we may write

$$E = \frac{V_c - V_a}{V_c + V_a} \cdot \frac{RT}{nF} \ln \frac{C}{C_1}$$

<sup>18</sup> *Zeit. phys. Chem.*, 4, 129 (1889)

$V_c$  = migration velocity of cation

$V_a$  = migration velocity of anion

$C$  = concentration of solution  $c$

$C_1$  = concentration of solution  $c_1$ .

If  $V_c$  is greater than  $V_a$ , a difference of potential will exist between the two solutions. The dilute solution side will be electro-positive to the concentrated solution side. If  $V_a$  is greater than  $V_c$  the opposite electrical orientation will result. If  $V_a$  is equal to  $V_c$  no potential difference will exist between the two solutions. In nearly all cases investigated the electrical orientation has been found to conform to Nernst's values for free diffusion.

In a few exceptional cases, the electrical orientation has not been in accord with this formulation. In such cases it seems probable that electrical influences, caused by adsorbed ions, operating within the pore, so affected the relative diffusion velocities of the ions that the usual type of potential orientation was not obtained.

*In the development of our theory we shall assume that the electrical orientation of the cell system is due to unequal diffusion velocities of the ions, and further that the relative diffusion velocities may be altered through the influence of adsorbed ions.*

#### CAPILLARY POTENTIAL

##### THE ELECTRICAL ORIENTATION OF THE PORE WALL SYSTEM

Quincke was the first to undertake an extensive study of diaphragm currents. He forced liquids through porous diaphragms and noted that differences of potential were produced. He believed that in some way the liquid bathing the pore wall became electrically charged by contact.<sup>19</sup> Later Helmholtz<sup>20</sup> through mathematical treatment developed an hypothesis to the effect that in nearly all cases solids and liquids, through contact, become electrically charged. The surface of the solid will be charged with a sign opposite to that of the more mobile layer of liquid near it, and thus will give a definitely oriented electrical double layer.

A potential difference set up at the end of the capillary

<sup>19</sup> *Ann. Physik.*, **107**, 1 (1859); **110**, 38 (1860)

<sup>20</sup> *Ann. Physik.*, **7**, 337 (1879)

pores of a diaphragm should cause, then, a displacement of this electrically charged layer of liquid along the capillary wall. Under a constant driving potential the flow of the liquid layer along the capillary wall will become continuous, and, provided the diameter of the pore be sufficiently small, liquid as a whole will be carried through the membrane by this moving liquid film.

Perrin<sup>21</sup> found that H and OH ions appeared to be especially active in bringing about an electrical double layer. He concluded that the sign of the charge of a body in a solution of electrolyte was attributable to a small preponderance of H or OH ions.

Somewhat later Freundlich<sup>22</sup> suggested that the electrical double layer was due to selective adsorption of ions and that ions other than H or OH may result in this so-called adsorption potential. Bancroft<sup>23</sup> has stated also that adsorption is a specific process and that the charge on a given substance depends upon the nature of the substance, and upon the nature of both cation and anion.

The general formulation expressing adsorption equilibrium<sup>24</sup> is  $\frac{X}{m} = \alpha C^{1/n}$

$X$  represents the amount of material adsorbed by  $m$  amount of adsorbent.  $C$  represents the concentration of material in the liquid phase. We may state, then, that the amount adsorbed is directly dependent upon the concentration of the substance in the liquid phase. In case we consider selective adsorption of ions from solution, we must consider an adsorption equilibrium for each ion<sup>25</sup>

as

$$\frac{XK}{m} = \alpha K C^{\beta K}$$

and

$$\frac{XA}{m} = \alpha A C^{\beta A}$$

<sup>21</sup> *J. Chim. Phys.*, **2**, 601 (1904); **3**, 85 (1905)

<sup>22</sup> *Kapillarchemie*, 1909, 245; *Z. physik. Chem.*, **79**, 407 (1912)

<sup>23</sup> *J. Phys. Chem.*, **19**, 394 (1915)

<sup>24</sup> *Z. physik. Chem.*, **57**, 385 (1907)

<sup>25</sup> Svedberg, Report of Faraday Society and the Physical Society of London, Oct. 25, 1920, p. 2,

In the further development of our theory we shall assume there exists an electrical double layer which is the result of selective ion adsorption. The ions opposite in sign to those adsorbed by the capillary wall reside in the movable liquid film. A movement of these ions in a direction parallel to the pore wall and toward one end of the capillary will result in movement of the liquid film.

#### ELECTRICAL CONDUCTIVITY BETWEEN THE TWO COMPARTMENTS OF THE CELL

In order to explain the mechanics of an anomalous osmotic system, by the electrical theory, it is necessary to consider the existence of a definite circuit or electrical conductor which will complete the cycle for the necessary electrical energy transfer. That is, some kind of electrical circuit independent of that represented by the free diffusion of ions is necessary in order to make possible a continuous flow of electrical energy from one compartment to the other—during the flow of liquid through the capillaries.

Freundlich,<sup>26</sup> in a paper in which he discussed the work of the writer, suggested that we might consider that the walls of the membrane serve as a conductor. This explanation, however, seems hardly satisfactory, as it is almost inconceivable that such poorly conducting substances as porcelain, gold beaters skin, and collodion, would serve as electrical conductors for this system.

In the theory herein presented, we shall postulate that the ions which form the effective electrical double layers function as electrical conductors. We shall assume that ions absorbed on the solid phase remain practically fixed in position and at the same time in adsorption equilibrium throughout the length of the pore, while ions of opposite sign, within the liquid film actually transport the current.

Were we to consider migration of adsorbed ions along the pore wall from concentrated to dilute solution with an attendant conduction of current, it would in no manner alter the theory. The electrical flow would still be in the same direction.

Our information relative to adsorption potentials is still too meager and uncertain to justify a definite conclusion as to the

<sup>26</sup> *Kolloid-Z.*, **18**, 11 (1916)

similarity between adsorption potentials and the potentials of reversible electrodes. While experimental evidence indicates that we may have movement of adsorbed ions as mentioned above, conclusive evidence is still lacking. We have on the other hand abundant proof of movement of the liquid film when subjected to a driving pressure of a difference of potential. Accordingly we shall assume that the electrical transport occurs through the migration of the ions within this film. During this migration the film itself is transported.

#### THICKNESS OF LIQUID FILM

Guoy<sup>27</sup> has stated that he believes the thickness of the liquid film will vary both with the electrolyte used and with its con-

#### REPRESENTATION OF CONDITIONS AT MEMBRANE PORE

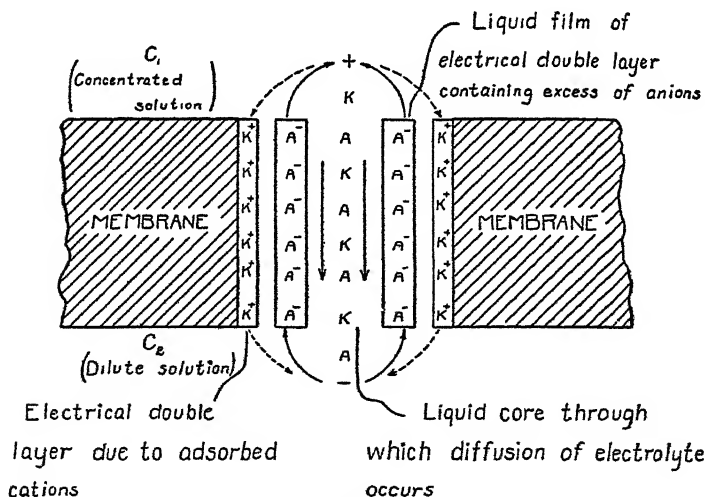


Fig. 7.

centration, the thickness decreasing markedly with increase in concentration of electrolyte.

<sup>27</sup> *Jour. Phys.*, 9, 457 (1910)

If we accept the view that the liquid film may have an appreciable thickness it would follow that the nature of the resulting osmose would be dependent largely upon the thickness of this film and the relation of this to the thickness or diameter of the remainder of the liquid in the pore which forms the core of the liquid column and through which, we assume, must occur the free diffusion of electrolyte downward.

This view is in accord with our results which show that the precise pore diameter is a most important factor in determining the type of osmotic effect.

#### THE COMPLETE ELECTRICAL CIRCUIT

Figure 7 represents conditions which according to this theory exist at a single pore of the membrane, when a solution of electrolyte  $KA$  is present. The concentrated solution is assumed to be in compartment  $C_1$  and dilute solution or pure water in compartment  $C_2$ .

In this case the anion,  $A$ , is represented as having the greater migration velocity which would result in a difference in potential for the membrane system, the dilute solution side  $C_2$  becoming electro-negative to the concentrated solution side  $C_1$ .

The cation  $K$  is adsorbed to a greater extent than anion  $A$ , resulting in an electrical double layer, the solid pore wall becoming thereby electro-positive to the liquid layer.

Anions  $A$  corresponding in number to adsorbed cations  $K$  reside in the liquid electro-negative part of the electrical double layer.

The difference of potential in the membrane system due to the difference in migration velocity of diffusing anions and cations will serve as a driving force to cause migration of anions ( $A$ ) held in the liquid film of the electrical double layer. This liquid film is assumed to be of appreciable thickness.<sup>28,29</sup>

A movement of anions in this film causes a movement of the film as a whole. Accordingly liquid is transported from compartment  $C_2$  to  $C_1$ . The return flow of anions tends to neutralize the effect of the membrane potential. However,

<sup>28</sup> Guoy, *Loc. cit.*

<sup>29</sup> Freundlich, "Physics and Chemistry of Colloids," Report of Faraday Society and Physical Soc. of London, 1921

the membrane potential will be maintained, though it will become increasingly less, so long as the solutions in  $C_1$  and  $C_2$  are of different concentration and diffusion of electrolyte continues.

We may consider that electrical energy is expended in producing work necessary to move the liquid layer.

#### SUMMARY AND CONCLUSIONS

We believe that the above theory explains, as no other theory has satisfactorily done, the cause of anomalous osmotic effects. With this theory, we can explain the fact that the tendency of flow of liquid through a membrane is in the direction demanded by the electrical orientation of an osmotic system. It explains equally well the effects of membranes so different in nature as porcelain, parchment paper, gold beater's skin, bladder, and collodion.

It explains also the cause of change in potential observed between solutions of different concentrations when a membrane is placed between these solutions. The electrical energy produced through the unequal migration velocity of ions from concentrated to dilute solution may be dissipated as work in moving the liquid film of the electrical double layer.

By application of this theory, we can account for the abnormal swelling or shrinking of colloid material. We need only to consider the operation of the forces as outlined above to explain the cause of penetration of the liquid into a gel or a flow of solution out from the interior of the gel.<sup>30</sup>

It is unnecessary at this time to discuss the relation of anomalous osmose to the realm of biological processes. It must be evident that if further investigation confirms the correctness of the theory outlined, we shall have a better understanding of biological processes and accordingly will have a working basis upon which further research should prove fruitful.

UNIVERSITY OF MICHIGAN  
ANN ARBOR, MICH.

<sup>30</sup> Bartell and Sims, *J. Am. Chem. Soc.*, **44**, 289 (1922)



DISCUSSION ON PAPER READ BY F. E. BARTELL

## MEMBRANE POTENTIALS AND THEIR RELATION TO ANOMALOUS OSMOSE

T. SVEDBERG: May I ask if according to the theory given by Dr. Bartell the osmotic flow was assumed to take place in such a way that a portion of the liquid core within the pore was not transported?

It seems that, according to the theory, all of the liquid in the capillary would have to be transported.

F. E. BARTELL: It is assumed that, provided the membrane pore be sufficiently small, the liquid column within the pore is transported as a whole due to the movement of the surrounding outer layer. In the case of a very large pore it is conceivable that the movement of the liquid film might not result in transport of the liquid column as a whole, but instead we might, owing to hydration of the diffusing ions have conditions approaching that of the old concept of simultaneous endosmotic and exosmotic currents. However, with membranes such as we have been using and with which we have obtained pressures of considerable magnitude, we assume that the entire liquid column moves in one direction, but that diffusion of electrolyte may occur through the core of this liquid column, and that the direction of this diffusion may be opposite to the direction of movement of the liquid in the pore.

T. SVEDBERG: I think it is extremely difficult to explain the phenomenon if we do not assume that the entire liquid is transported because the pressure obtained is based on the assumption that the whole core of the liquid is transported.

J. F. MCCLENDON: I wish to emphasize the importance of Dr. Bartell's work. We have been engaged in work related to anomalous osmose for a number of years and are consequently interested to hear of his recent work. It appears that Prof. Bartell has offered the first explanation which covers this complex problem satisfactorily.

In his experiments Prof. Bartell has clearly shown that osmose is directly related to electrical charge. Whatever the theory may be, the fact remains that potential differences do exist in such systems and that the flow of liquid conforms to the electrical orientation of the system.

It seems probable that the electrical factors must influence the diffusion of the solute, and that the diffusion of solute (electrolyte) through different membranes might be quite different owing to the electrical charges set up.

We might have the case of two vessels containing liquid separated by two different membranes, one of which would produce the electromotive forces required to cause movement of liquid and the other membrane with a selective permeability for the ion one wished to have diffuse against concentration. In this manner we might have a machine for concentrating an ion on one side of the membrane. I believe that the stomach offers an example of that kind. There we have membranes of different characters separated from each other so that they do not interfere with one another by immediately equalizing the concentrations in the neighborhood of the different membranes.

Upon this basis, for example, we do not need to assume that ammonium chloride is actually secreted as such within the stomach.

Let me repeat that Prof. Bartell has certainly contributed something valuable and I only wish I could express my appreciation of it in words that are suitable.

J. ALEXANDER: So far as I know there is not anything mysterious about the presence of acid in the stomach other than that its presence is due to a differential diffusion. I would like to inquire to what extent Dr. Bartell has considered this question.

F. E. BARTELL: Throughout the entire progress of our work we have kept the question of diffusion uppermost in mind as we believe it to be one of the main keys to the whole problem.

In this connection we have studied the relation of the Donnan membrane equilibrium theory to the distribution of electrolytes within our osmotic systems.

We have every reason to accept the fundamental principles of the Donnan theory. The acceptance of that theory in no way alters the theory I have presented insofar as the behavior of the fairly permeable membrane osmotic system is concerned. We assume that anomalous osmotic effects are due to the electrical orientation of the membrane system. The electrical orientation of the membrane is the result of diffusion of electrolyte, or we may say the spacial distribution of ions. The Donnan theory then may aid us in our future attempts to ob-

tain a strictly quantitative relationship between the various factors responsible for anomalous osmotic effects.

R. THIESSEN: The discussion so far has concerned for most part theoretical things. I would like to ask Dr. Bartell for facts concerning the actual structure of the membrane itself. I would like to know the method used in measuring pore diameters, something about the relative size of the pores, the nature of a pore, and the exact structure of the membrane as this is very important.

F. E. BARTELL: I agree with the last speaker that the facts to which he referred all have an important bearing. I fear, however, it would take considerably more time than I have at my disposal to answer these questions at all in detail.

In 1909 I published (with Prof. Bigelow) the first of our work on the pore diameter of membrane pores; the results of this work appeared in the *J. Am. Chem. Soc.*, 31, 1194 (1909); the work has been continued and most of the later papers have appeared in the *Journal of Physical Chemistry*. Our most satisfactory method has been based upon an application of Jurin's Law. The pores of a membrane are filled with water and the pressure necessary to force the water out is determined. Knowing these pressures the pore diameters may be calculated.

In a recent paper (Bartell and Carpenter) we have shown that pore diameters obtained from a method based upon Jurin's Law and from a method based upon Poiseuille's formula show closest agreement for collodion membranes.

In a paper recently presented to one of our journals we have shown that in the case of collodion membranes we can obtain membranes of almost any desired porosity, that we can actually regulate the distribution of the pores and further that we can be assured of a very uniform distribution of them.

As I pointed out in my paper, membranes of porcelain, parchment paper, gold beaters skin and collodion all show effects which are very similar. It seems probable that the pores in a collodion membrane are quite uniform in size while in the case of porcelain, owing to the difference in size of the grains of the membrane material, we undoubtedly have pores varying considerably in size. In stating pore size of our membrane we refer to the diameter of the largest 200 pores in an area of 1.54

cm<sup>2</sup>. There are undoubtedly many other pores within this area with diameters much less than this. We believe that the larger pores are mainly responsible for the anomalous effects while it seems probable, from our work with the fine-grained porcelain, that anomalous effects are far less marked with membranes having fine pores.

A. R. JOHNSON: I think the matter of pores is important. Suppose you have a case in which a membrane separates a solution of tartaric acid from its solvent. Given active and non-active tartaric acid, we find that one acid will pass through and the other will not. In case the pore size is the same in each instance how does it happen that one kind of acid will pass while the other kind will not? How does it happen that a certain particle will digest tartaric acid while another will not? How can a purely mechanical operation explain those facts?

F. E. BARTELL: Unfortunately I do not happen to be familiar with the facts just stated so do not feel qualified to advance an explanation. I suppose we might fall back upon that most convenient phenomenon, adsorption, which serves us so well in "explaining" many of the little understood processes, and say that the adsorption of these two different acids by the membrane material may be different.

J. A. WILSON: Dr. Bartell made reference to the Donnan theory. I would like to point out that in the Donnan theory we deal with one of the effects and not the movement of the fluid. In case of a protein solution, with increasing concentration of HCl we get the water to flow first in one direction then in the other. I would like to know if your theory can account with any degree of definite accuracy as the Donnan theory does for that movement?

F. E. BARTELL: As yet we have done no strictly quantitative work in an attempt to relate the magnitude of the different electrical forces to the magnitude of anomalous osmose. Qualitatively and even semi-quantitatively there is a close relationship. We have not, and cannot with our present data show what may be termed precise quantitative relationships. Our results do account for the direction of osmotic flow and in a manner which I do not believe possible with an application of the Donnan theory alone. In explaining the osmotic processes in protein systems I believe it is generally assumed that some of

the protein material is dissolved within the cell and that this material functions osmotically.

J. A. WILSON: In the case of a jelly that is not true; that assumption is not made.

F. E. BARTELL: It seems probable that a system of that type might offer apparent exceptions and in that connection I may state that I do not consider our anomalous theory as it stands sufficiently comprehensive to explain *in toto* the swelling and shrinking effects noted in gels.

However, in the swelling and the shrinking of gels I believe we may have what we can term anomalous swelling and anomalous shrinking, a sort of superimposed effect and that we invariably do encounter these effects whenever electrolytes are present in the solution. Assuming a gel has been allowed to swell in pure water then is placed in a solution of an electrolyte an abnormal swelling effect would correspond to a negative osmotic action while a shrinking effect would correspond to, and in fact would probably be caused by, an abnormally positive osmotic action.

E. F. BURTON: I would be pleased to know how that charge on the wall of a membrane pore was measured and also to know the reason for the change in charge.

F. E. BARTELL: We have used two different methods for determining the sign of the charge on the pore wall, namely, the electrical osmose method in which the membrane was used with different solutions of different concentrations and the direction of flow of solution determined under the influence of an impressed electromotive force, and the cataphoresis method in which the membrane was finely ground then subjected to ordinary cataphoresis experiments in the solution in question. To take a specific example of the latter method a porcelain membrane was finely ground and suspended in pure water. The particles under the influence of electrical potential appeared to be charged negatively, accordingly we considered the pore wall to be electro-negative to water.

The addition of a small amount of acid caused the particles to become less negative while a still higher concentration of acid caused the particles to reverse their former direction of migration indicating that they had become charged positively.

In all cases we assumed the pore wall of a membrane to bear

a charge of the same sign exhibited by the membrane material when suspended in a solution of approximately the same composition as that of the solution within the pore.

E. F. BURTON: How about collodion?

F. E. BARTELL: Collodion was found to be electro-negative in all our tests. We were unable to reverse the sign of the charge even with high concentration of acid.

T. SVEDBERG: If I understand Dr. Bartell right, the size of the pores was a very important factor. I wonder if Dr. Bartell has been able to measure the percentage of pores of different sizes.

F. E. BARTELL: Measurement of pore diameters of collodion membrane indicates a close uniformity of pore size throughout. In the case of porcelain we have shown that a large number of the largest pores have practically the same size while there are many more present which are much smaller.

T. SVEDBERG: It is not the average size that is important but rather the distribution of sizes.

F. E. BARTELL: Our results indicate that when the pore diameters of the membranes with which we have worked are below a certain limiting value we will obtain positive osmose, while it is only with membranes having pore diameters greater than this that negative or anomalous osmotic effects are obtained. I prefer to accept the view that in practically all cases we have present a tendency to produce normal osmose, that there is a tendency for the solution to obey the gas laws, but superimposed upon this we may have the tendency to produce anomalous effects. The latter effects may be due largely to the presence of the larger pores in the membrane.

E. O. KRAEMER: I should like to ask Dr. Bartell how he considers that the motion of the ions in the movable layer of the electrical double layer brings about the movement of the liquid associated with the movable layer when the oppositely charged ions in the center of this core move in the opposite direction but do not move the liquid in the core. Why do we not have a balancing effect? In any case, how does the motion of the ions lead to a motion of the liquid?

F. E. BARTELL: I believe it is generally accepted in the theory of electrical osmose that we have migration of ions with the liquid film and that they are held in this film by the attraction of a corresponding number of ions adsorbed on the walls

of the membrane pore. If they are held in the electrical double layer in that manner it does not seem necessary to bring difficulties upon ourselves by trying to relate these ions to an equilibrium with the ions within the liquid core which are obeying the laws of dilution and diffusing toward the more dilute solution through this core.

E. O. KRAEMER: But the question still remains, why the motion of an ion in one direction leads to a transport of liquid, while a motion of an equivalent number of ions in the other direction does not lead to a motion of so much liquid.

Also, I do not understand how it is that when you reverse the charge on the pore wall the ions which were passing through the center and did not transport liquid now do so; why should that change take place?

F. E. BARTELL: The assumption is not made that the ions diffusing through the liquid core are active in transporting the liquid as a whole but rather that liquid transport is caused by the movement of the liquid film, which in turn is probably caused by the ions held therein. A reversal of sign of the electrical double layer, other factors remaining constant would result in reversal of direction of movement of the liquid film and consequently a reversal of the direction of flow of solution. We assume that the liquid film within the pore forms a sort of tough skin which transports the liquid within; in fact we assume that the liquid film may be of considerable thickness and that its influence may in some cases extend quite to the center of the liquid core.

E. K. CARVER: It seems that the answer to the question is that in the center of the liquid core there are ions of each sign going in opposite direction, whereas, on the walls the ions are of the same sign, moving just as the walls of the tube would move, in one mass.

E. O. KRAEMER: I do not think that is the case. The current through the core would, I believe, tend to transport liquid with it.

L. H. REYERSON: I would like to suggest that the motion of the ions can only be possible if the liquid is not a perfect dielectric. If the idea just presented is correct we could perfect a perpetual motion machine: we would have the whole riddle of perpetual motion solved.

E. K. CARVER: It seems to me that the answer to the perpetual motion machine idea would be that it would not work, due to the fact that the transference numbers of the ions passing through the pores are different, so that there would be a change in influence which would eventually stop the machine.

F. E. BARTELL: The last remark is clearly to the point. In order to obtain an electromotive force we must have a difference in the migration velocities of the ions diffusing through the core of liquid from concentrated to dilute solution. It is the work of diffusion which really brings about the electromotive force necessary to cause movement of the liquid column. Further, the difference in potential between the two faces of the membrane would become less as the concentration of the solutions on the two sides became nearly the same.

We may assume that the electrical energy tends to flow on its return circuit through the medium of the ions in the liquid film of the electrical double layer and that in this manner we may consider that electrical energy is converted into the work of moving the liquid column as a whole.

In the majority of cases the electrical sign existing between the two faces of the membrane is that expected from a consideration of the relative migration velocities of the ions. In a few cases at certain concentrations of solution the electrical sign is not that to be expected. In the case of sodium hydroxide with porcelain at 0.2 *N* NaOH concentration, the dilute solution side is electro-negative to the concentrated side, as it should be in free diffusion, while with a more dilute solution 0.01 *N* NaOH the dilute solution side is electro-positive. We have at this time no explanation to offer for this type of orientation. We do find, however, that the direction of flow of solution is as demanded by the electrical orientation of the system.

A. L. FERGUSON: In connection with this subject there is another factor which may play a part in producing anomalous osmotic effects and that is the neutralizing effect of the diffusion potential.

The difference in potential on the two sides of the membrane is undoubtedly due to unequal diffusion of positive and negative ions. It seems to me that we must account for the disappearance of this potential and that we may do so by assuming that greater adsorption of ions on the membrane pore occurs



on or towards the end occupied by the more concentrated solution. This would result in a higher adsorption potential on that end, with the result that there would be a tendency for a neutralizing effect of these two types of potentials.

F. E. BARTELL: I believe that is probable; undoubtedly much depends upon the adsorption potentials when we get down to the final analysis; however, at the present time we know far too little about absolute values of adsorption potentials to warrant far-reaching conclusions involving those potentials.

## SURFACE FILMS AS PLASTIC SOLIDS<sup>1</sup>

BY ROBERT E. WILSON AND E. D. RIES

### INTRODUCTION

The original object of the work described in this paper was to secure a more satisfactory explanation for the stability of soap bubbles and to determine the essential reason for the marked differences between various soaps and other colloidal solutions in their ability to produce permanent foam. In view of the interesting results obtained in this field the work was extended to a brief study of interfacial films in emulsions and of films adsorbed on solid surfaces.

The remarkable stability of some bubbles is shown by the fact that Sir James Dewar was able to preserve large soap bubbles for as long as nine months. An explanation frequently given for the stability of such bubbles is that the solutions have a surface tension far lower than that of water. Actually, however, surface tension in itself has little, if any, effect on the stability of the bubbles, though theoretically it would slightly decrease the amount of energy required to form them. The lack of any definite relationship is shown by the fact that pure liquids with equally low surface tension do not foam, and that even in the case of aqueous solutions the stability of the foam is by no means proportional to the amount of lowering of the surface tension, as will be brought out in the later discussion.

A realization of these facts has led a number of investigators to attribute the stability of bubbles to a high superficial viscosity, due to the well-known tendency of colloidal substances to concentrate at the interface. Indeed, as far back as 1870 Plateau<sup>2</sup> pointed out the existence of very high superficial viscosities in soap solutions, and later Luvini,<sup>3</sup> Stables and Wilson,<sup>4</sup> and Lord Raleigh<sup>5</sup> compared these viscosities for

<sup>1</sup> Presented in preliminary form before the General Meeting, American Chemical Society, at Rochester, N. Y., in April, 1921; in final form before the Colloid Symposium, Madison, Wis., in June, 1923

<sup>2</sup> *Poggendorff Ann.*, **141**, 44 (1870)

<sup>3</sup> *Phil. Mag.*, **40**, 190 (1870)

<sup>4</sup> *Phil. Mag.*, **15**, 406 (1883)

<sup>5</sup> *Proc. Roy. Inst. G. Brit.*, **13**, 85 (1890)

different solutions by measuring the force required to move bodies of various shapes through the surface of the solution. Probably the most promising method was that used by Stables and Wilson, which consisted of rotating a disc as a torsion pendulum in the surface of the solution. They found that the superficial viscosity of some solutions was more than a thousand times that of water, and pointed out the probability that this was related to the stability of bubble films.

Even this, however, is not an entirely satisfactory explanation. If we consider the cross-section of a small bubble highly magnified (Fig. 1), it becomes clear that the main force tending to destroy the bubble is the tendency of the solution to run down and thin out the film near the top of the bubble to such a point that it will break. This is exactly the mechanism observed



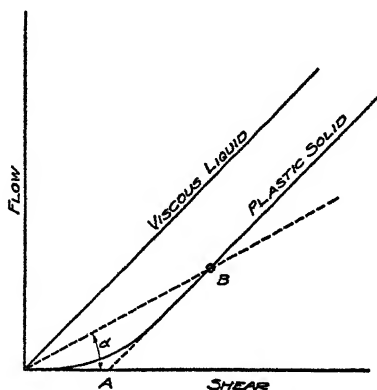
*CROSS SECTION OF SMALL BUBBLE, HIGHLY MAGNIFIED*

*FIG. 1*

in breaking bubbles—a very thin dark spot forms near the top of the bubble shortly before rupture takes place. It might, of course, be argued that capillarity would hold the thin film of solution in place, but this could not be effective unless the walls of the capillary were rigid or held apart from collapsing by some force of appreciable magnitude. Mere viscosity might slightly delay thinning out, but could not possibly account for bubbles lasting for days or weeks, to say nothing of months. This is borne out by the fact that heavy lubricating oils may readily have a surface tension as low as that of soap solutions and a superficial viscosity of the same order of magnitude, and yet have no tendency to form highly stable bubbles, though the bubbles do require somewhat longer to break than similar bubbles in a lighter oil.

From the foregoing it should be clear that what is really needed to explain the stability of soap bubbles is the existence

of some force in the walls of the bubble which can indefinitely resist the force of gravity or prevent the thinning out of the bubble by capillary forces. In other words, to explain the stability of bubbles it is only necessary to assume that the walls of the bubble possess the properties of a solid, rather than of a liquid, however viscous. The same thing would presumably be true of the surface layer of solutions which tend to give stable foams. Even this point of view is not new, as Lord Raleigh has stated his belief that certain surface films were really solids. It has, however, never been proven quantitatively.<sup>6</sup>



COMPARATIVE FLOW CURVES  
FOR A VISCOUS LIQUID AND A PLASTIC SOLID

FIG. 2

## THE DETERMINATION OF THE PHYSICAL PROPERTIES OF SURFACE FILMS

### 1. Theory

If the surface films of colloidal solutions are indeed solid, they certainly belong to the class ordinarily known as plastic solids, which will flow when subjected to large shearing forces, but which are able to resist small forces indefinitely without

<sup>6</sup> Langmuir has proven, to be sure, that a monomolecular film of stearic acid on water was a solid with a definite melting point, but he was dealing with films which were essentially separate phases adsorbed on the surface of the water, and not with colloidal solutions

any flow taking place. The relationship has been brought out very clearly by Bingham<sup>7</sup> as applied to paints and many types of colloidal suspension or emulsion. When such a plastic solid is forced through a capillary under different shearing stresses the relationship between flow and shear is essentially that brought out by the lower curve in Fig. 2, as contrasted with the upper line for a viscous liquid where the flow is directly proportional to the shear and the viscosity is defined by the ratio of shear to flow (in proper units), or the cotangent of the angle made by the line with the X axis.

In the case of the plastic solid, flow does not, in general, take place until the amount of shear known as "yield value," A, is reached, and beyond this point the flow is substantially proportional to the shear minus this yield value. If an attempt is made to measure the apparent viscosity when the shear has a given value such as that corresponding to point B, the ratio of this force to the observed flow, or the cotangent of the angle  $\alpha$ , might by analogy be termed the "apparent viscosity" of the plastic solid under these conditions. If, however, the flow had been measured at any other value of the shear, the apparent viscosity thus determined would obviously be greater at the lower values of the shear or less at the higher values. Indeed, just this behavior on the part of plastic solids is largely responsible for unsatisfactory results obtained in attempting to control the physical properties of such substances by viscosity measurements.

It might then be stated as a characteristic property of a plastic solid, as distinct from a viscous liquid, that the apparent viscosity, or shear-flow ratio, of the former increases fairly rapidly as the shearing stress decreases. In applying this to surface films it is obviously not feasible to force them through a capillary, but any other measurement of apparent viscosity should bring out the same essential variation with shear. It was therefore decided to modify the torsion pendulum arrangement of Stables and Wilson to make it an accurate measure of superficial viscosity, different shearing stresses being obtained by allowing the amplitude of the swings to decrease gradually. The resistance to rotation is, of course, measured by noting the

<sup>7</sup> "Fluidity and Plasticity," McGraw-Hill, 1922

rate of damping of the swings, the relationship being essentially as follows:

If a torsion pendulum is rotating in a viscous medium, the frictional force of retardation should be proportional to the product of the viscosity of the fluid times the average rate of motion. Since the period is constant, the average velocity is in turn proportional to the amplitude of the swing. The amount of work done against friction is proportional to the moment of inertia of the system and the decrease in the amplitude of the swings. Since the frictional force is proportional to the amplitude, as pointed out above, the percentage (not absolute) decrease in the amplitude of the swings should be constant or, in other words, the *difference* between the *logarithms* of the *amplitudes* of successive swings should be *constant*. For convenience this latter term is referred to as the log decrement.

Stables and Wilson have formulated this expression mathematically, essentially as follows:

$$d = \frac{Vt}{kI_0} \quad (1)$$

where  $V$  = viscosity

$I_0$  = polar moment of inertia of the disc

$d$  = log decrement

$t$  = the period of swing

and  $k$  = an experimentally determined constant

This may, of course, be rearranged to the form

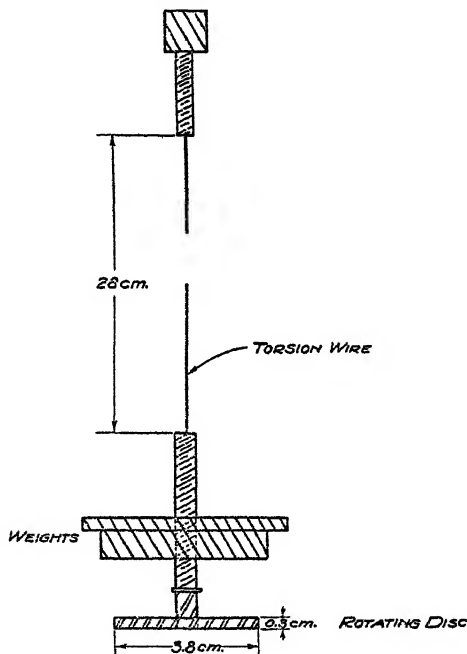
$$V = \frac{k d I_0}{t} \quad (2)$$

and once  $I_0$  and  $k$  have been determined for a given apparatus, the viscosity of any other fluid may be determined by measuring  $d$ .

If the apparent viscosity of the medium is constant regardless of the amplitude of the swings, the log decrement should be constant, and hence a plot of the logarithm of the amplitude against the number of swings should give a straight line whose slope is a measure of the viscosity. If, however, the apparent viscosity tended to increase as the shear (in this case determined by the amplitude) decreased, the logarithm of the amplitude should drop off more and more rapidly as the number of swings increased and this would result in a curved line convex upwards if the results are plotted by the above method.

## 2. Apparatus

Fig. 3 shows a diagram of the rotating disc together with its wire and support. The lower disc was glass with its circumference ground and was fastened into the brass support. This latter was made so that lead discs could be placed upon it to vary the moment of inertia. The wire was steel piano wire about 24 gage. The top support was set into a collar



APPARATUS FOR MEASURING APPARENT VISCOSITY OF  
SUPERFICIAL LAYERS

Fig 3

so that by turning it torsion could be put on the wire and the disc caused to turn. A crystallizing dish held the solutions and the whole was contained in a glass cabinet to decrease evaporation and temperature changes. To the lower support was fastened a mirror which reflected a spot of light onto a curved scale at 1 m. radius on which the amplitudes were read.

### 3. *Materials Used*

The following substances were used in the investigation: sodium stearate and sodium oleate (Merck); Quillaja saponin (Mallinckrodt); and commercial Turkey-red oil neutralized with NaOH to pink with phenolphthalein as indicator.

The solutions were made up in concentrations of 1 in 1000 and used as stock solutions. The desired concentrations were obtained by dilution with freshly distilled water. The stock solutions were kept until they showed signs of turbidity which was usually within three or four days. The distilled water used was freed from  $\text{CO}_2$  as completely as possible by boiling, as this gas precipitated the substances out of solution, particularly sodium stearate.

It was found that with certain of the substances the age of the solution, either stock or dilute, had a marked effect on the formation and properties of the film. Consequently it was necessary especially with saponin to use fresh stock and fresh dilute solutions for each run in order to obtain reproducible results.

### 4. *Experimental Procedure*

Before runs could be made on the colloidal solutions it was necessary to determine the various moments of inertia and to calibrate the instrument with non-colloidal substances of known viscosity.

Since the lower support was non-homogeneous its moment of inertia could not be accurately calculated. It was therefore obtained by the following experimental method:

Let  $T$  = the period of the glass disc and support  
and  $I_1$  = the polar moment of inertia of the same

$$\text{Then} \quad T = 2\pi\sqrt{\frac{I_1}{c}} \quad (3)$$

$$\text{or} \quad I_1 = \frac{T^2 c}{4\pi^2}$$

where  $c$  is a constant depending on the length, diameter and nature of the torsion wire.

Let  $t$  be the period when a disc or ring of known moment of inertia,  $I_2$  (as determined below), is placed on the support.

$$\begin{aligned} \text{Then} \quad t &= 2\pi\sqrt{\frac{I_1 + I_2}{c}} \\ \text{or } I_1 + I_2 &= \frac{t^2 c}{4\pi^2} \end{aligned} \quad (4)$$



Substitution for  $c$  from (3) and rearranging gives

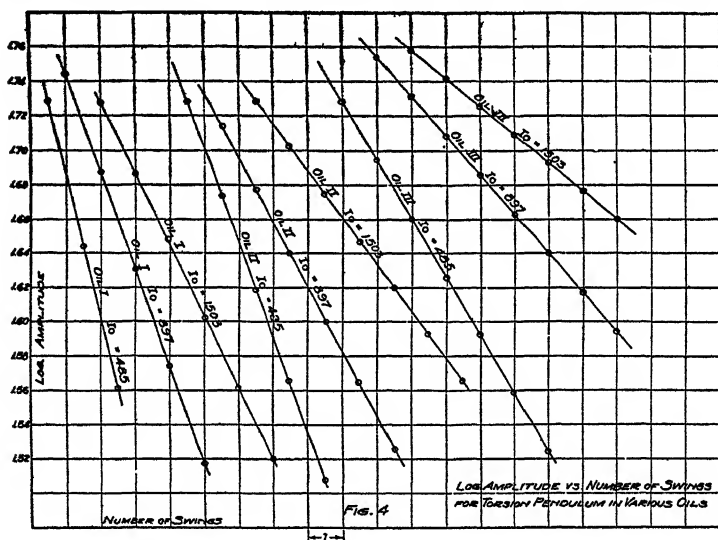
$$I_1 = I_2 \frac{T^2}{t^2 - T^2}$$

and for  $I_1$  from (3) gives

$$c = \frac{4\pi^2 I_2}{t^2 - T^2}$$

Since  $I_2$  is known we can determine  $I_1$  and  $c$  by measuring  $t$  and  $T$ .  $c$  varies slightly with the load on the wire but it was found that any changes were less than the accuracy of measurement.

The polar moments of inertia of the metal discs and rings were calculated on the assumption that they were homogeneous



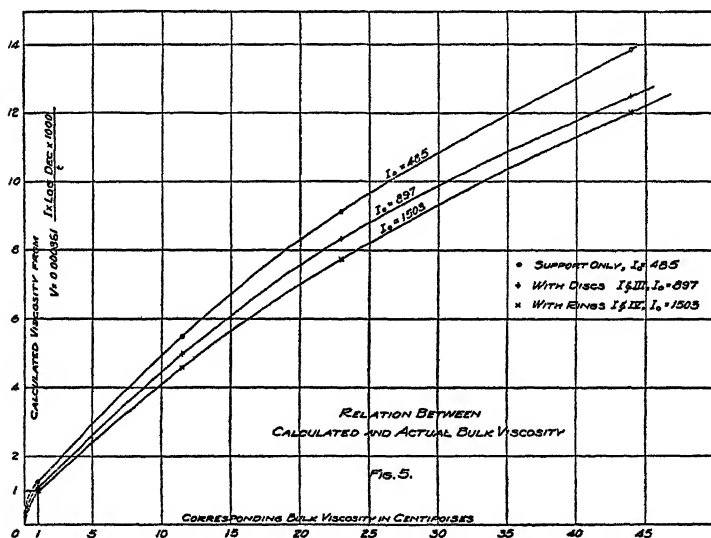
and regular in shape, an assumption which was found accurate by checking the discs one against another.

By making measurements on a variety of combinations the moment of inertia of the glass disc plus support was readily determined to be 485 gr. cm<sup>2</sup>. In the following tables and figures the total polar moment of inertia of the whole system is always reported.

The instrument was then calibrated and the validity of the Stables and Wilson equation tested by measuring the decrements in air and in liquids of known viscosity including water

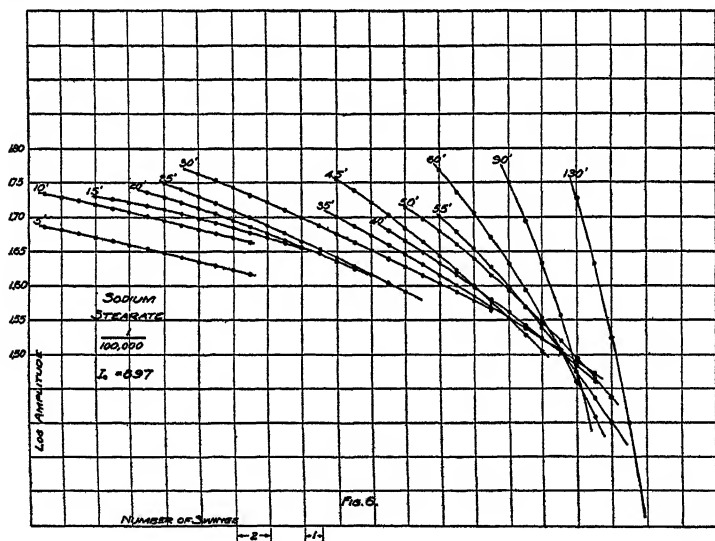
and oils of several different viscosities. Several different discs giving different moments of inertia were also used. Fig. 4 shows the results of a few typical measurements. It will be noted that in all three cases the rate of decrease of the log amplitude is constant as demanded by theory.

From the slope of these lines (equal to the log decrement) values of  $k$  could be calculated. Unfortunately, however, it became evident that Equation 1 did not represent precisely what happened and hence the values of  $k$  determined under different conditions were by no means constant. In order to show the divergences, the value of  $k$  (0.000861) deter-



mined at the highest moment of inertia with water as the fluid was used in Equation 1 to calculate the viscosities of the other fluids, and these calculated viscosities were plotted against the actual bulk viscosity in Fig. 5. It will be noted from this that the values of  $k$  obtained in a given fluid with pendulums of different moments of inertia agree fairly well, but that the log decrements, and hence the calculated viscosities, are by no means proportional to the true bulk viscosities. Part of this is due to the failure to take into account the rate of damping *in vacuo*, due to internal friction in the wire, but there was no obviously satisfactory method of making such a correction.

However, the results of the experiments on the colloidal substances used in this investigation have been arbitrarily calculated by this equation, simply to give a means of comparison. The "apparent viscosities" obtained are really not true viscosities, but are proportional to the energy consumption necessary to distort the surface films. Such energy consumptions are enormous compared to those which occur when the disc is rotated in a viscous liquid, since apparent viscosities of 50, such as were found with sodium stearate, would require an impossible extrapolation of the calculated viscosity *vs.* bulk viscosity curves. This is even more remarkable since it is

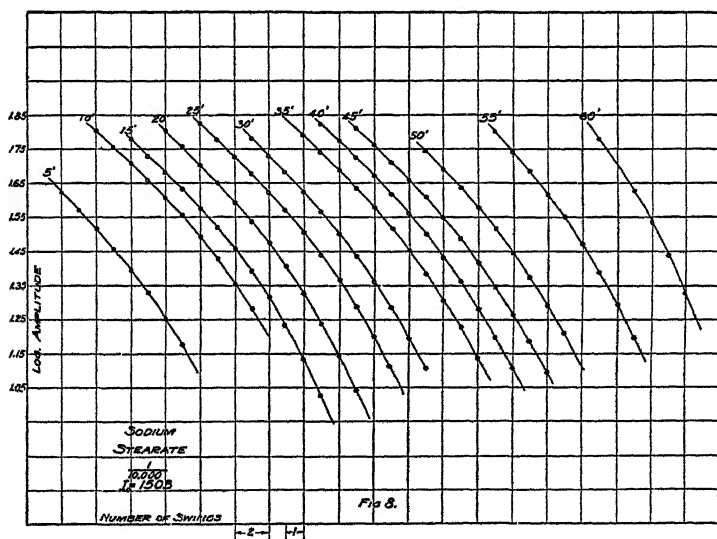
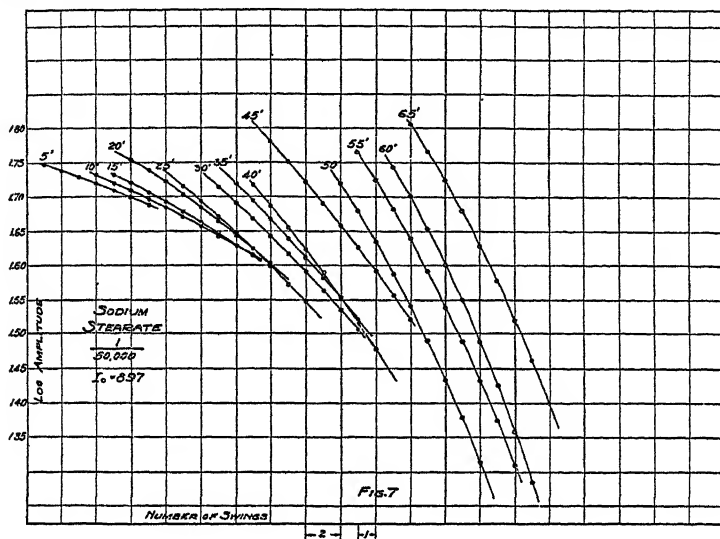


exerted by a film which is much thinner than the amount of fluid which was effective in retardation when the disc was rotated in oil.

The calculated viscosities are therefore to be considered as merely a means of comparison between the various substances.

One further preliminary experiment was performed to determine whether the size of the dish had any effect on the readings obtained. Measurements were made on water and on oil in two different dishes, one about four inches and the other about six inches in diameter. The slopes of the lines for each liquid were identical for both dishes. Hence the size of the

dish used—between those limits—has no effect on the readings. In the subsequent experiments the four-inch dish was used so as to require less solution.

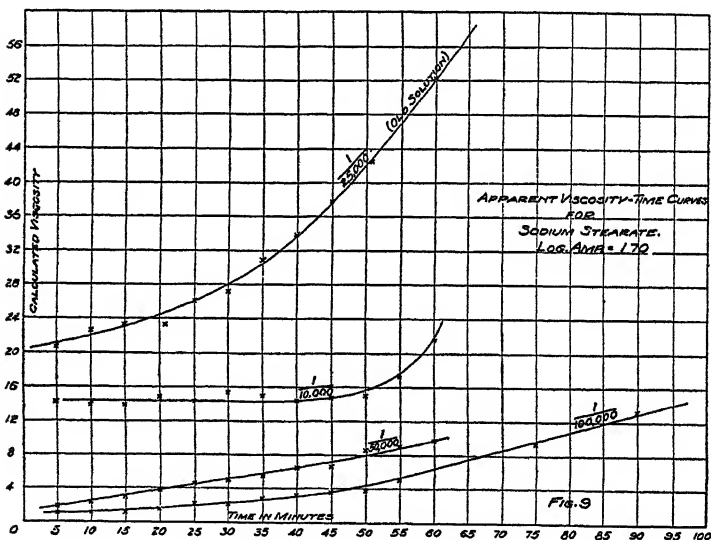


In all studies on colloidal solutions the sample to be tested was withdrawn from the center of a nearly filled volumetric

flask just after vigorous shaking, and delivered to the carefully cleaned dish, using an amount just sufficient to come to the top edge of the rotating disc without covering it. Since the films changed in their properties with time, observations were taken by starting the pendulum swinging at about the same amplitude every five minutes after the sample was delivered into the dish.

#### 5. Results of Torsion Pendulum Measurements

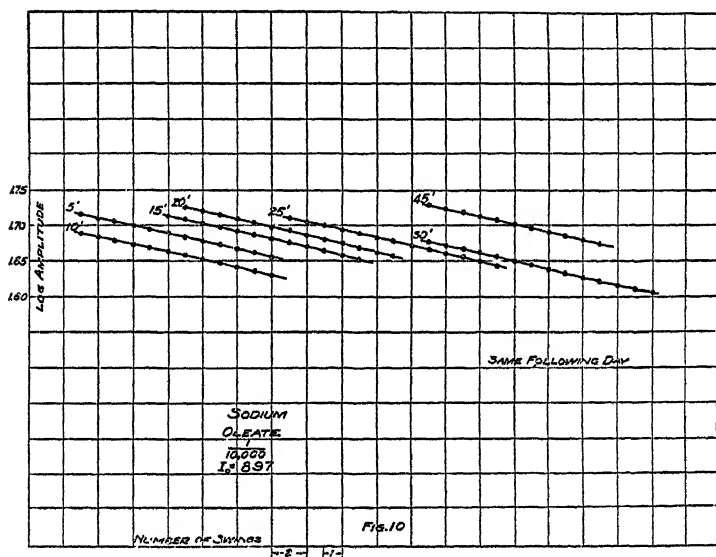
Figs. 6, 7 and 8 show typical results obtained on sodium stearate solutions of three different concentrations. Without entering into a detailed discussion, a study of these curves brings out three interesting facts, as follows:



- Practically all the lines are markedly curved, indicating that the surface film of even a 1 to 100,000 solution of sodium stearate is a plastic solid and not a viscous liquid.
- The slope of the curves increases greatly with time, showing that the film builds up rather slowly.
- The higher concentrations build up films more rapidly, and eventually give much stronger films.

In order to show more clearly the change in the apparent viscosity with time after a fresh surface has been formed, the slopes of each of the curves were determined at a given ampli-

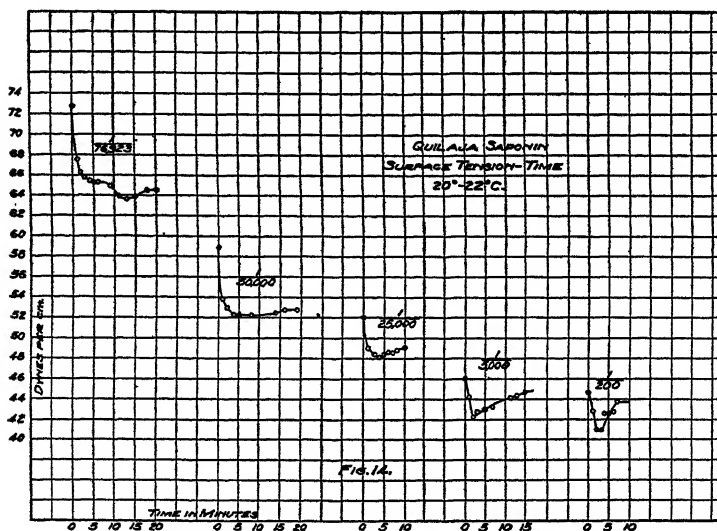
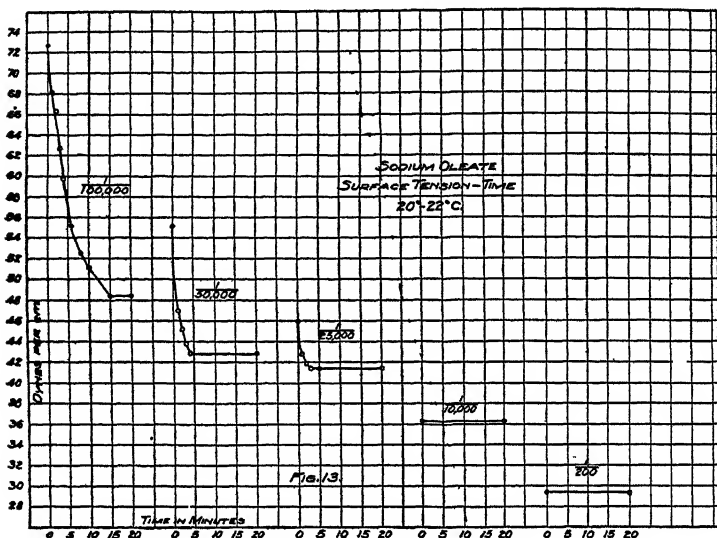
tude ( $\log. \text{amp.} = 1.70$ ) and the apparent viscosities calculated from these data, giving the three lower curves in Fig. 9. This figure also gives a similar curve for a 1 to 25,000 solution of sodium stearate which had stood in a stoppered flask after dilution for several days before testing. As was always found to be the case, this solution gave a much higher initial and final viscosity than those given by fresh solutions. A few attempts were made to study this phenomenon, but it was found very difficult to get reproducible results on any except fresh solutions tested on the same day they were diluted. Even the strong stock solutions of sodium stearate changed on standing, though more slowly than the dilute solutions.



Sodium oleate solutions gave results of quite a different character. Fig. 10 gives results for a 1 to 10,000 solution which are typical of this and lower concentrations. All solutions in this range give lines which are straight, do not change with time, and have a slope but little greater than pure water. When a concentration of 1 to 5000 is reached, however, the results in Fig. 11 are unmistakable evidence of the building up of a plastic solid film of quite appreciable strength.

As a plausible reason for the marked difference in the behavior of the two closely related solutions, might be mentioned

is generally considered to be the best foam producer, even though it is much poorer in equivalent low concentrations.

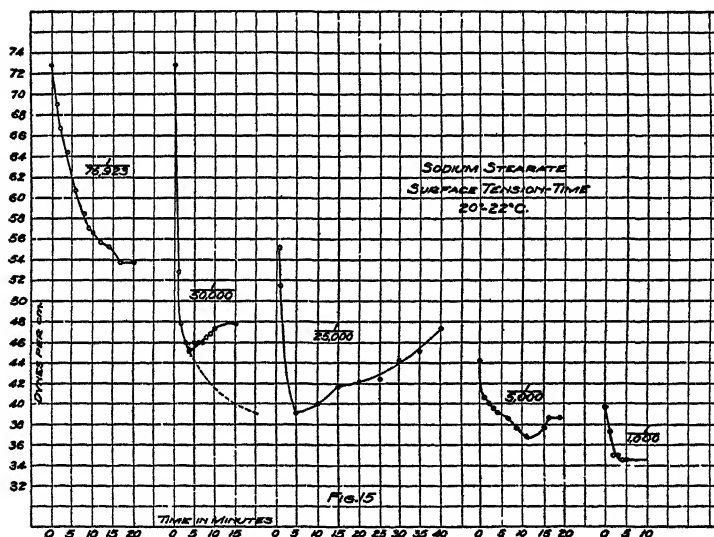


As far as they go, the foregoing results certainly seem to substantiate the concept of a plastic solid surface, rather than

any surface tension or viscosity effect, as the main factor in producing stable bubbles. It was considered desirable, however, to study these films by other methods and obtain further data as to their physical properties and behavior.

#### THE EFFECT OF PLASTIC SOLID FILMS ON SURFACE TENSION MEASUREMENTS

Since plastic solid films appear to be present on the surface of many colloidal solutions, the question arose as to whether their existence might not interfere with the measurement of surface tension by the customary methods, such as the drop weight or du Nouy. In the latter method, for example, when



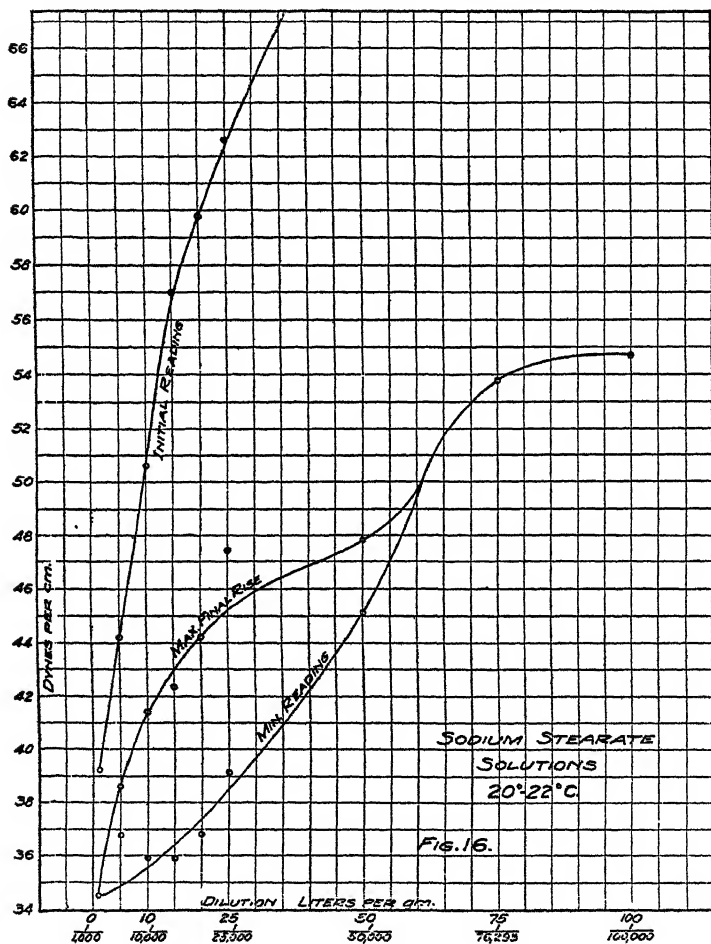
the ring is lifted from the surface of such a solution it would have to overcome not only the reversible force involved in the surface tension of the films, but also the frictional force corresponding to the yield value of the plastic solid surface film, and this should have a considerable magnitude when the film had become very strong with increasing time.

A series of measurements was therefore made by Mr. Charles B. Dicks<sup>8</sup> in this Laboratory on the surface tension of various colloidal solutions by the du Nouy method, using in general

<sup>8</sup>Undergraduate thesis, Mass. Institute of Technology, 1921



the same substances and similar concentrations to those employed in the above work. Measurements were made on each solution at short time intervals after the formation of a fresh surface. The results of these measurements are shown in Figs. 13-16 inclusive and are, indeed, striking confirmation of the



results obtained by the other method. In dilute solutions of all the colloids the surface tension at first falls off rapidly with time, due to the time required for the colloid to diffuse to the surface and give the equilibrium or static value of the surface

tension. The sodium oleate (Fig. 13) eventually reached an equilibrium value such as would be expected.

In the case of saponin and sodium stearate, however, a point is soon reached where the surface tension passes through a minimum and then rises again. Such an apparent spontaneous increase in surface energy is on its face a contradiction of the laws of thermodynamics, but it can readily be explained on the assumption that the true surface tension continues to decrease beyond this apparent minimum point, though at a comparatively slow rate, as indicated by the dotted line on the 1 to 50,000 curve in Fig. 15. Throughout this period, however, the yield value of the plastic solid surface film has been increasing until it becomes of the same order of magnitude as the surface tension forces themselves, and the continued increase in this yield value more than makes up for the decrease in the true surface tension. Only the fortunate fact that at certain intermediate concentrations the solid film was increasing greatly in strength after the true surface tension ceased to drop rapidly, made it possible to obtain the minima in the curves measuring the combined effects. The absence of a minimum would not necessarily mean the absence of a plastic solid film.

The times required to build up these films are of the same order of magnitude as those observed by Ries, although the work was done independently and with different solutions at different times.

Also, the work was unfortunately done before the importance of the "age of solution" effect was appreciated, and most of the solutions used by Dicks were made up several days before they were tested. Fresh solutions were found to give similar curves, though with somewhat less pronounced minima.

When the higher concentrations were reached the films were formed much more quickly and there was little change in surface tension after the first measurement. In the case of oleates, and also of a few measurements on Turkey-red oil, there was no minimum observed at any concentration. All these facts are, of course, in quite satisfactory agreement with the concept of a plastic solid surface film, and with the indication that sodium oleate has much less tendency to form such films than saponin or stearate.

It is indeed surprising that phenomena of this magnitude,

which appear to vitiate any ordinary surface tension measurements on such solutions, have apparently escaped attention. Quite similar discrepancies would certainly be observed in the drop weight method of measuring surface tension and probably also in the capillary rise method.

#### MEASUREMENT OF THE THICKNESS OF THE PLASTIC SOLID FILMS

It seemed highly improbable that forces of magnitude observed by the foregoing methods could be produced by any film of molecular dimensions, such as are ordinarily referred to in considering surface tension phenomena. An attempt was therefore made to determine whether or not the solid film was of microscopic dimensions. This was done by arranging an ultra-microscope so that it focused on the surface of a sodium stearate solution containing some precipitated barium sulfate. At first the colloidal particles of barium sulfate were observed to be in violent Brownian motion, but in a few minutes after preparing the fresh surface this was replaced by a slower vibrational movement in which all the particles in the field moved in unison, as if suspended in a jelly. The microscope was then lowered with a micrometer attachment until a zone was reached where Brownian motion was still taking place. In a few minutes more, the Brownian motion would again give way to the oscillatory motion, which gradually decreased in amplitude, but could be set up again by any slight jar. By gradually screwing down the microscope and following this moving boundary, the rate of solidification of these surface films could be followed in a very satisfactory manner, and again a film was observed to be gradually building up for as much as an hour after a fresh surface was formed, even though precautions were taken to prevent evaporation. The final thicknesses observed in the different solutions varied from 10 to 40 microns.

These dimensions are enormously larger than even the large molecules present in soap or saponin, and indicate that the phenomenon is essentially a colloidal one. The concentration of such colloidal particles is, of course, quite different from the distribution of dissolved molecules which can be predicted from the Gibbs equation. The precise forces which cause this concentration into such thick layers are admittedly rather

obscure. It can scarcely be a gravitational phenomenon, as has been suggested, since the true density of sodium stearate and sodium oleate is known to be well above 1, although precise data are lacking.

There is an interesting parallelism in structure and stability between the plastic solid bubbles studied in this work and the very stable "armor plated" bubbles produced in ore flotation, where the bubble surface is frequently found to be filled with solid particles in contact, which give the bubbles great stability.

#### APPLICATION TO LIQUID-LIQUID INTERFACIAL FILMS

In view of the interesting results obtained on surface films, an effort was made to see if similar evidence could be secured to demonstrate the existence of plastic solid interfacial films in stable emulsions.<sup>9</sup> The work along these lines was carried out in this laboratory by Allen Abrams and has not yet been published. This article presents merely a brief summary of results of this work which will probably be published in detail in the near future.

A series of careful drop weight measurements were made on Nujol and castor oil in a series of solutions of sodium oleate, sodium stearate, saponin and Turkey-red oil, to see if there was any minimum in the drop weight curves when plotted against the time of formation as observed in the case of surface films, but no such behavior was observed. The only indication of plastic solid films found in the course of these measurements was in the case of sodium stearate where the highest concentration used (0.18%) gave a slightly higher interfacial tension than intermediate concentrations (0.10–0.12%) for both Nujol and castor oil. This might be explainable, however, on the basis of the formation of slightly supersaturated solutions at the intermediate concentrations which were precipitated out at higher concentrations. Solutions made up hot always gave lower surface tension values initially than after standing for 24 or 48 hours.

For the reasons cited previously, the absence of minima in the time curves did not disprove the possibility of the presence of plastic solid films at the interfaces, and the attempt was

therefore made to find some different methods of settling this point. The outstanding difference between the forces of surface tension and those inherent in a plastic solid film is that the former are perfectly reversible, whereas the latter are frictional in character and hence irreversible. If a small drop of oil (less than a hemisphere) were started at the end of a capillary immersed in a solution of an emulsifying agent, a certain force would be required to make the drop grow, and if the pressure of the oil at any moment dropped below the value necessary to cause the drop to grow, it would immediately begin to contract, since the forces are reversible. If, however, there were a plastic solid film surrounding the oil globule, there would be quite an appreciable range where the size of the drop would not change as the pressure was decreased, since the plastic solid film would tend to prevent collapse until its yield point was exceeded.

Since the pressures required to produce drops under such conditions are very low, accurate measurements thereof would be difficult. The idea occurred, however, that the same effect could be produced by making one drop work against another. This was accomplished by breaking a capillary off at right angles and sealing it into the apparatus shown in Fig. 17 in such a way that the two broken ends of identical size formed the tips of the double capillary. Since the pressure due to surface tension inside a drop is inversely proportional to the radius of curvature of the drop, if a small drop were connected to a larger one the tendency would be for the small drop to disappear and flow over into the larger one. If the tips of the capillary were in the same horizontal plane and the oil heavier than water, this tendency would be slightly augmented by the fact that the center of gravity of the large drop would be somewhat lower than that of the small drop. The latter effect was largely eliminated by adding enough  $\text{CCl}_4$  to the oils to make them just slightly denser than water (about 1.01). If the forces involved are reversible, this absorption of the smaller drop should take place very rapidly, being opposed only by the friction through the capillary, and this was found to be the case for drops of oil ( $+\text{CCl}_4$ ) in plain water. If, however, irreversible frictional forces are present and are of the same order of magnitude as the reversible forces, drops of nearly the same

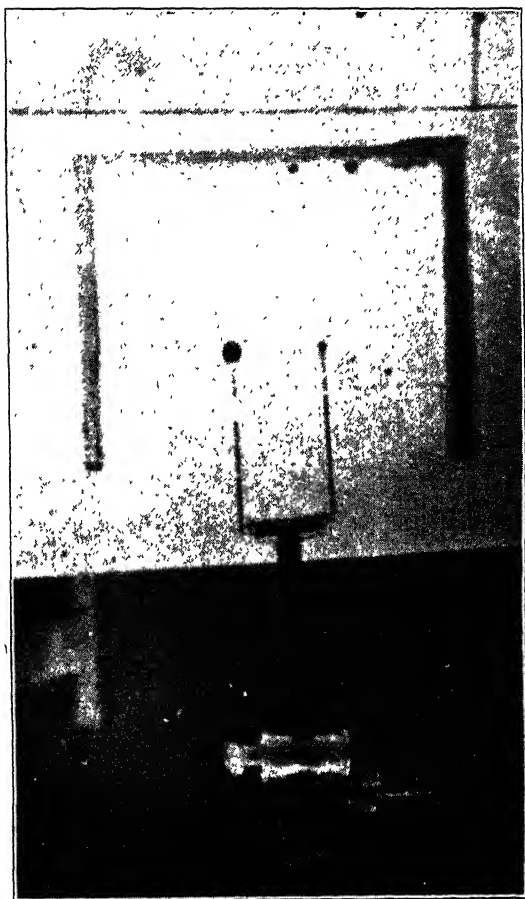


Fig. 17

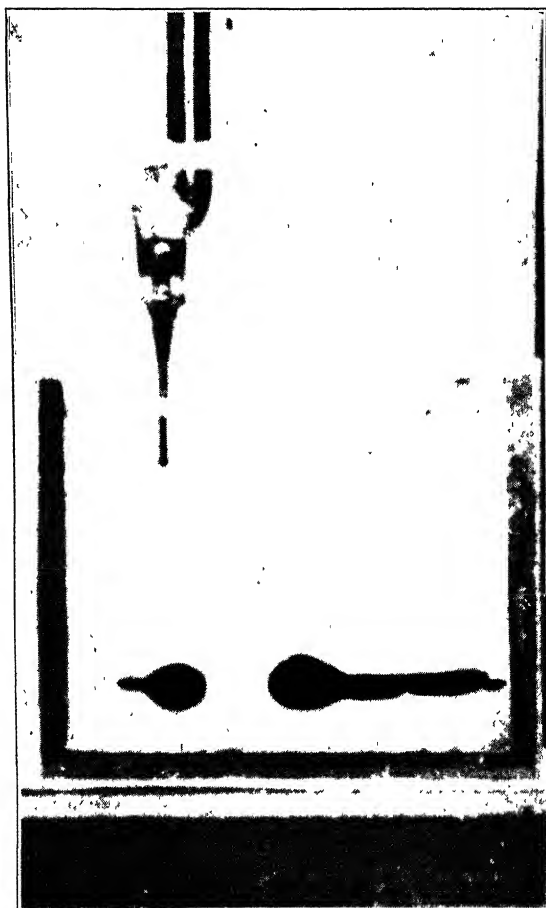


Fig. 18

size might remain connected indefinitely without absorption of the smaller.

Tests were carried out using most of the combinations employed in the above mentioned drop weight work, except that  $\text{CCl}_4$  was added to the oils as stated above. In carrying out the tests the stopcock was opened to allow drops to form very slowly on both tips. One drop was then removed, and the stopcock opened fairly wide to form two drops of unequal size on the two tips. The cock was then quickly closed and the diameters measured approximately by sighting against a scale just behind them. Observations of the two diameters were then taken at various time intervals, generally until absorption was complete. It was found that most emulsifying agents considerably retarded the reabsorption of the smaller drops, but that only in comparatively few cases was reabsorption entirely prevented. A conspicuous example of this was a 1 to 1000 solution of saponin, in which no reabsorption took place, even if the large drop was 50% greater in diameter than the smaller one, and the two allowed to stand connected for many hours.

The drops formed under these conditions also had very peculiar properties in that they maintained irregular shapes and even sharp points for long periods of time, again indicating that plastic solid forces of great magnitude were present. A photograph of some of these peculiarly shaped drops, taken by Mr. E. C. Crocker, is shown in Fig. 18, the first of these being obtained by allowing the drop to fall on a salt solution denser than the oil. The photographs were taken thirty minutes or more after the formation of the drops.

Comparing these results with those obtained on the surface of colloidal solutions, it would appear that there is less tendency to form plastic solid films at interfaces than at free surfaces, although they are undoubtedly formed in some of the more concentrated solutions of saponin and sodium stearate. Lower concentrations give films of high apparent viscosity, but if they have a definite yield point characteristic of plastic solid films, it must be small compared with the forces of surface tension at concentrations below 1 to 5000.

One factor which might account for the greater apparent difficulty in getting evidence of the presence of plastic solid



films between liquids is that all the surfaces studied in this case were curved, whereas the surface films previously investigated were plane. It is conceivable that the films might show much greater evidence of solidity in two dimensions than in three, on account of their thinness. It would be very desirable to extend this investigation by studying plane horizontal interfaces by the rotating disc and ultramicroscopic methods described above in their application to surface films.

#### PLASTIC SOLID FILMS IN LUBRICATION

In view of the foregoing results, it seemed probable that plastic solid interfacial films might play an important part in lubrication. In a journal bearing operating normally the metal surfaces are separated by a true fluid film dragged in by the rotation of the journal, and the only property of the lubricant which affects the friction is its viscosity. However, at very slow speeds or high loads, where the true fluid film has not formed, or is too thin to completely separate the surfaces, another property of the lubricant, termed "oiliness" for want of a better name, shows up, in that oils of identical viscosity give quite different coefficients of friction. This difference has generally been attributed to the formation of an adsorbed film of molecular dimensions. An extensive investigation was carried out in this laboratory to determine whether the characteristics of these films were similar to those of the plastic solid surface films in stable bubbles, etc. The results of this study have already been published,<sup>10</sup> but the essential conclusions may be summarized briefly. From experiments on:

1. The static coefficient of friction between metals lubricated with different substances;
2. The coefficient at low speeds and high loads;
3. The rate of building up of electrical resistance between two polished metal surfaces exposed to oils for varying lengths of time before squeezing together;
4. The rate of clogging of metal capillaries through which different oils were passed; it was concluded that the adsorbed films which were effective in inducing friction at low speeds and high loads were:

<sup>10</sup> Wilson and Barnard, "The Measurement of the Property of Oiliness," *J. Ind. Eng. Chem.*, **14**, 682 (1922); *J. Soc. Automotive Engrs.*, **11**, No. 2, 143 (1922)

- (a) of colloidal rather than molecular dimension;
- (b) plastic solids in their resistance to displacement;
- (c) built up slowly, requiring a matter of many hours to reach full thickness.

It will be noted that these properties are all very similar to those found to be true of surface films on bubble-forming solutions. Another point of similarity was found in the fact that some materials which were strongly adsorbed at the surface of the metal, but which did not form plastic solid films, tended to raise rather than lower the coefficient of friction. Fatty acids and oil-soluble soaps were the most effective materials in increasing oiliness.

It was also found that by shaking an oil up for some time with a considerable mass of pyrophoric iron, the film-forming constituents could be removed almost completely, and later recovered, together with considerable oil, by extracting the iron with solvents.

#### SUMMARY

1. The reason for the marked stability of the bubbles from some colloidal solutions has been shown to lie in the fact that the surface films are gel-like plastic solids, rather than viscous liquids.

2. The failure of other solutions with low surface tension to give stable bubbles is due to the fact that they give only fluid films.

3. The plastic solids are of colloidal, rather than molecular dimensions, and require a matter of hours to build up to maximum strength.

4. Solutions which form plastic solid films give erroneously high surface tension results by the du Nuoy and presumably by other methods of measuring the surface tension, because the yield value of the plastic solid film is added to the true reversible surface tension.

5. There is evidence of similar behavior in the case of some liquid-liquid interfacial films in emulsifying agents, but the production of such films appears to require much higher concentrations than in the case of surface films.

6. Plastic solid films of similar properties were shown to play an extremely important part in lubrication, being the

determining factor in the oiliness of a lubricant which reduces friction at low speeds and high loads.

DISCUSSION ON R. E. WILSON'S PAPER

SURFACE FILMS AS PLASTIC SOLIDS

W. V. EVANS: I would like to ask Dr. Wilson if he has any measurements as to the effect of different metals on the thickness of this film, and why the film reaches a maximum thickness that is not monomolecular?

R. E. WILSON: Regarding your first question, the differences between steel and brass were appreciable, but by no means large. The only metals tested which did not form rather thick films were aluminum and magnesium, which presumably had a layer of oxide on their surfaces.

W. V. EVANS: The other question I asked was—what would be the explanation of the fact that the film builds up to a certain thickness and then stops?

R. E. WILSON: One of the reasons I came here was to find out why it does stop. I confess I can offer no satisfying explanation at the present time.

W. V. EVANS: May I ask you also just what you think the thicknesses of the films are?

R. E. WILSON: On metals, sometimes as high as one-tenth of a millimeter. The more firmly adherent portion of value in lubrication is probably a matter of 10 or 20 microns thick.

H. N. HOLMES: In an experiment that I performed recently I took a quantity of gum dammar in benzene and then added a very large drop of water. Within a matter of a few seconds one could see an opalescent film, which would wrinkle as the beaker was tilted. Now that film was of very appreciable thickness. When I used several large drops of water and allowed both liquids to evaporate, big, milky shells of the gum dammar were left. I have the feeling that there we have a balance of forces between what you might call a coagulating influence from the water on this peptized colloid and the peptizing action of the benzene on the other side of the film. I think that could account for having thicker films in some cases than in others.

J. ALEXANDER: Are you familiar with the patents of Southcombe and Wells? According to them, fatty acids greatly increase the lubricating power of oils, and the question is whether there were not free fatty acids in the oils which you used. Were these mineral oils that you used absolutely pure petroleum oils?

R. E. WILSON: Yes.

J. ALEXANDER: No sign of any free acids in them?

R. E. WILSON: No.

S. E. SHEPPARD: I would like to ask Dr. Wilson a question or two in relation to the film formation and the gel structure. Dr. Wilson suggested a parallelism to some extent between gel formation and plastic films, and mentioned the case of gelatin. Now, Metcalfe some years ago showed that surface rigidity was possessed by colloid solutions, particularly by peptone solutions. Peptones result from the breakdown of gelatin, and it is a fact that the foaming power increases very considerably, while the rigidity of the jelly as a whole may be entirely destroyed. If this plastic film is formed in that way the gel structure must be of a totally different order than in a gelatin jelly. I think that the type of plastic film that is formed here is very definitely related to the recent work on the structure of the so-called liquid crystals. It has been shown that in the soap films a structure is formed that may be likened to a pack of cards, such that the mono- or di-molecular layers can slide very readily over each other, and this has been demonstrated in the case of a certain number of the bodies forming so-called liquid crystals. Practically all the substances that have been described by Dr. Wilson are of the character that form long-chain molecules, which allow liquid crystal formation. These substances form two entirely new phases of matter called mesomorphic, which have perfectly definite transition points. The plastic film here would be associated in every case with the shearing of layers, which are not, however, like the layers of a liquid that is capable of movement in every direction, but are layers that can move in one direction only. In the movements that Dr. Wilson used to investigate the depth of the film, I do not know whether he observed anything there similar to that observed by Perrin in regard to Brownian movements in soap films. There may be an indication of a certain ease of

motion in one direction in two dimensions, but practically absolute rigidity in the other dimension.

L. S. PALMER: I take it that Dr. Wilson does not assume that it is necessary to have thick films at these interfaces to get the solid plastic structure. You could have it at even one molecule thick, but you haven't the methods to measure it. That probably clears up the point that Dr. Sheppard mentions. You might assume that you could watch down to perhaps even a molecule thick. I don't know that you could.

R. E. WILSON: One remark in reply to the question of Dr. Sheppard first: I did not observe whether the motion was in two dimensions or in three, but if there were such a rigidity in two dimensions and not in the third, it would explain the difficulty we had in getting evidence of plastic solid films at liquid-liquid interfaces. In our drop experiments we always had curved surfaces and these might be much less rigid than if spread out in a plane. What we should do is to rotate our disc in a plane surface between two liquids.

E. K. CARVER: In regard to the thickness of that film, I was wondering if possibly the current could have anything to do with it, and if the measurements were made while a slight current was passing through from one metal to the other that might throw some light on this.

R. E. WILSON: Our experiments showed clearly that the current did not form the film—indeed, it was found that alternating current would either disrupt them or destroy their resistance. The details of these measurements are given in my paper on the measurement of oiliness.

H. S. TAYLOR: I think the most significant factor in connection with this lubricating difficulty is the fact that the film did not form on the glass. It did form on the true metal surfaces. In that connection I would like to ask whether an oil which had been freed from its "oily" constituents would recover this property in time.

R. E. WILSON: If exposed to the air, it would recover it to some extent.

H. S. TAYLOR: I think that the film formation might be due to surface catalysis; possibly the slow rate of formation of the film may be due to a formation of an oxidized oil which has properties different from that of the hydrocarbon itself. There

is a possibility that oxidation may account for the formation of that film.

R. E. WILSON: Yes, but you take an oil and add to it stearic acid or calcium oleate and you get films built up very quickly of different thicknesses and sizes.

H. S. TAYLOR: That does not introduce any difficulty because you always get a layer on the surface, and that adsorbed layer may be built up relatively slowly.

R. E. WILSON: But the point is you get films of the same thickness.

H. S. TAYLOR: I feel quite sure that there is a definite energy potential drop there from the first oil.

R. E. WILSON: Of course this is a matter of thousands of molecules, not four or five. I agree with you entirely for four or five, but not in this case.

# FORCES REGULATING THE SIZE OF COLLOIDAL PARTICLES

BY E. F. BURTON

All the methods of preparation of colloidal solutions of whatever kind may be divided into two classes as was, I believe, first pointed out by Professor Svedberg<sup>1</sup> himself, *viz.*, dispersion methods and condensation methods. One of the processes consists in the particle being built up by the condensation of molecules of materials to form a nucleus which grows to a certain limiting value and then stops growing; the other process consists of an automatic breaking down of a large mass into smaller and smaller units until, when a certain size is reached, the disintegration ceases and the particles under given conditions remain of constant size. It is the purpose of the present paper to discuss briefly the physical (or chemical) causes which might regulate this limiting size.

In the first place I might recall to you that in colloidal solutions we are dealing with a particular range of sizes, which are bounded on the lower side by what can be rendered visible in the ultramicroscope, say to  $10^{-7}$  cm., in diameter, and on the upper side by the size which in any given case will settle out of solution under gravitation. A simple calculation, using Stokes' law, will give the rate of fall in water of silver particles (of density assumed equal to that of solid silver, 10.5) having diameters given in Column I of Table I, as recorded in the table.

Radius	Vel., cms. per sec	Time to fall 1 cm.
1 cm.	200,000	0.000005 sec.
0.1	2,000	.0005 "
.01	20	.05 "
.001	2	5 "
.0001	0.002	500 "
.00001	.00002	50,000 sec. = $\frac{1}{2}$ day, app.
.000001	.0000002	5,000,000 sec. = 58 days app.

It so happens that the range between these slow falling particles and those which we can just see in the ultramicroscope is a comparatively limited range and there is no particular

<sup>1</sup> Svedberg, "Herstellung der Kolloide," Dresden, 1909

reason why, for some solutions, the limiting size of growth might be either below our lowest limit or above our highest.

As a second preliminary point, I may say that the questions to be discussed in this paper are not the reasons for the stability of these solutions. Of course, the limiting size is fundamentally the reason for the stability, but more particularly I think most of us will agree that the possession of an electric charge ultimately prevents the particles increasing in size beyond a certain limit, while the molecular motions of the medium, giving rise to the Brownian movement, entirely masks any slight tendency to settle due to gravitation.

Perhaps it will be best to confine ourselves to the simplest possible colloidal particle, say such as gold, silver, or platinum in a Bredig sol (in water).

According to Professor Svedberg's work,<sup>2</sup> these colloidal particles are due to the condensation of the metallic vapor and consequently we shall have to begin our investigation by considering the mutual action of a few molecules brought close together. The X-ray work of Debye and Scherrer<sup>3</sup> has shown that colloidal particles of gold, silver, etc., are really collections of small crystals completely similar in form to the ordinary macroscopic crystals of the metals. The forces regulating the arrangement of these molecules will be those functioning during the formation of ordinary crystals. The electronic view of the structure of atoms would lead us to believe that atoms can exert forces along different directions and the lines of direction of these forces determine the geometrical form of the crystals.

A very illuminating sidelight on the importance of these crystal forces in the building up of the colloidal particle is formed in the effect of the medium surrounding a crystal on the crystal habit, as pointed out by Wherry.<sup>4</sup> For example, on tabulating the impurities affecting the habit of sodium chloride crystals, it is found that alkaline solutions seem to produce octahedrons and acids, cubes. Much work along this line has been done by Marc<sup>5</sup> and Niggli.<sup>6</sup> Wherry suggests that through

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<sup>2</sup> Svedberg, "The Formation of Colloids," Churchill, London, 1921

<sup>3</sup> Zsigmondy, "Kolloidchemie," 3rd ed.

<sup>4</sup> Wherry, Private communication: To appear in *Proc. Mineralog. Soc. Amer.*

<sup>5</sup> Marc, Series of papers in *Z. physik. Chem.*, 1910 to 1913

<sup>6</sup> Niggli, *Z. anorg. Chem.*, 110, 55 (1920)



the existence of unsatisfied valences extending upward from the surface of the crystal, a given impurity is absorbed most strongly on certain faces and plate these faces; then, if the impurity is in sufficient amount, the plated face may remain while all others disappear through the crystal's further growth. Many instances are known of the great effect of impurities present in the medium during the formation of colloidal particles and these effects may be due to the habit of the microscopic crystals making up the colloidal particles.

We have not as yet definite evidence as to whether there is any directional law acting when the submicroscopic crystals come together to form the larger ultramicroscopic particle. This colloidal particle must be built up by the conglomeration of large numbers of small sub-microns into single particles which we see. If we imagine two such sub-microscopic crystals coming together we should expect that the crystal directional forces should be less effective than when individual crystals are merely adding single molecules to themselves. We have then to consider a second series of forces, which have to do with the growth in these larger masses, the forces of surface tension.

In dealing with the effects of surface tension we are groping in the dark to a certain extent. We have experimental knowledge of the phenomenon of surface tension for comparatively large surfaces. A very interesting question is: "Is there a lower limit to the size of surfaces to which we can apply the ordinary surface tension laws, *e. g.*, that  $(T \times A)$  tends to become a minimum?" The so-called Law of Curie<sup>7</sup> regulating crystal growth, *viz.*, "that the crystal grows in such a manner that  $\Sigma(T \times A)$  taken for all faces is a minimum" was disproved by Gibbs, and according to Wherry is not in accordance with observations. The ordinary surface tension theory of Laplace is, as is well known, that the surface phenomena are due to some special state induced in the surface molecules due to unequal attraction inwards and outwards from the surface. This theory contemplates a surface with millions of molecules. What happens when a few molecules come together? Many important practical effects of surface tension, *e. g.*, ore flotation, are still enigmatic.

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<sup>7</sup> Curie, P., *Bull. soc. franc. minéral*, 8, 145 (1880); see Tutton, "Crystallography," Vol. I, p. 25 (1922 ed.)

We are all familiar with the late Lord Rayleigh's<sup>8</sup> method of determining an upper limit to molecular diameters by measuring the thickness of a film of oil which spreads over the surface of clear water. Some inactive powder, *e. g.*, lycopodium, is sprinkled over the surface to indicate motion and a small drop of oil is touched to the surface; immediately the lycopodium powder shoots away from the point and it appears that the oil spreads in a uniform thin layer over the surface. However, if this clear space is viewed through a microscope, it will be found to be dotted thickly with minute globules of oil which are in constant motion. The same forces which prevent a long cylinder of liquid being stable, prevent the existence of a thin lamina of oil on the surface; one cannot tell exactly whether all of the oil is collected in the globules or not.

The motions which take place in particles of microscopic sizes are extremely violent and experiment points to the existence of very formidable surface tension forces acting upon very small particles. When two masses coalesce the change in the potential energy is given by  $(T \times dA)$  and therefore the action would depend on the area of the whole mass compared to the original area. The mechanical effect of bringing two masses together would be given by  $F = ma$  or  $\alpha = \frac{F}{m}$ .

Now the masses vary as  $a^3$ , and if the  $F$  varies as  $a^2$  consequently  $\frac{F}{m} = \alpha$  varies as  $a^{-1}$ . That is, surface tension action on small masses is much more violent; the acceleration  $\alpha$  for  $a = 10^{-4}$  cm. would be of order 1/100 of  $\alpha$  for value of  $a = 10^{-6}$  cm.

It seems safe to assume that the conglomeration of sub-microscopic crystals of a substance is regulated chiefly by the fundamental surface tension law, *viz.*  $(T \times A)$  tends to become a minimum. Definite optical experiments on the shapes of colloidal particles seem to indicate that they are usually spherical.

The question now arises "Why does this automatic conglomeration continue only until the particles reach a given size, which may be different for given substances under varying conditions?" There cannot be any doubt that for such solu-

<sup>8</sup> Lord Rayleigh, "Scientific Papers," Vol. III, No. 183, p. 347

tions as the Bredig sols and, perhaps, for suspensoids in general, this cessation of growth is due to the electrical charges possessed by the particles.

It might be well to recapitulate our present position with regard to the charge possessed by colloidal particles.

1. *Mobility*: we might say that these particles are charged because they move in an electric field.<sup>9</sup>

2. *Source of charge*: as to the source of the charge there is much doubt, due to the fact that we find that particles in un-ionized liquids become charged as well as in ionized media.

3. *Particles and ions*: it is an experimental fact which is not often accentuated that the mobility of these particles is very little less than the ordinarily accepted mobilities of electrolytic ions. For example, the mobilities of potassium ions and gold colloidal particles are nearer one another by far than the mobilities of potassium and hydrogen ions. In addition to this the relation of mobility to viscosity of the medium is the same in the case of colloidal particles and ordinary ions.<sup>10</sup>

When we come to deal with the theoretical side of mobility we find explanations offered which are quite unsatisfying. The dominating idea is that of the Helmholtz double layer theory according to which the colloidal particle is the core of two concentric layers of unlike charges, the inner layer on the material of the particles and the outer layer due to oppositely charged ions attracted to the solid core from the surrounding medium. In most references to this double layer theory, the outer layer is treated as being closely situated to the inner core, the whole being a neutral entity. We have been in the habit of following Lamb<sup>11</sup> in treating these two concentric spheres as a condenser, *i. e.*, two concentric spherical surfaces a very small distance apart. This conception leads to a very fantastic accounting of the motion of the particles in an electric field (Helmholtz) and also to the denial of the mutual action of two charged particles (Porter).<sup>12</sup>

There can be very little doubt that colloidal particles do exert forces of repulsion on one another which can be accounted

<sup>9</sup> Burton, "Physical Properties of Colloidal Solutions," Chap. VII, p. 132 (2nd ed.)

<sup>10</sup> Burton, *loc. cit.*, p. 143; see also *Z. Elektrochem.*, 26, 424 (1920)

<sup>11</sup> Burton, *loc. cit.*, p. 134, *et seq.*; Lamb, Brit. Assoc. Advancement Sci. Reports, 1887, p. 495

<sup>12</sup> Porter, "Law of Distribution of Colloidal Particles," *Trans. Faraday Soc.*, 1922

for if we assume that there is a resultant charge (positive or negative) on the entity (colloidal particle + outer Helmholtz layer), as a whole. This view seems to be more in keeping with our ordinary idea of phenomena depending on the action of electrolytic ions. Assuming that the central solid core, for some reason or other, has a charge, it is not reasonable to suppose that there will be attracted and held to the immediate neighborhood of its surface a sufficient number of oppositely charged ions to neutralize entirely the charge on the particle. Ions in the outer layer will be diffusing to and fro from the core and at any instant there will be a state of statistical equilibrium, with the net result that there will be present in the immediate neighborhood of the particle a resultant charge which may be such that there will be repulsion between the neighboring particles, and such that any one particle will move in an electric field. This view has already been suggested by W. C. Lewis<sup>13</sup> in order to account for discordant values of  $e$ , the charge on a colloidal particle.

A glance at the results of various workers will show us that there appears to be for every kind of suspensoid under given conditions a certain limiting concentration of the particles in the medium. The writer<sup>14</sup> has worked this out for Bredig silver sols and finds that apparently the closest approach which one particle can make to its neighbor is of the order of 50 times the diameter of the particle. Continued arcing in any sample merely results in increasing the coarse residue at the bottom of the containing vessel. This is exactly what should be expected in the case of mutual repulsion of the particles.

In his work on the distribution of colloidal particles in a vertical column, Perrin<sup>15</sup> finds the same law of distribution as applied to the case of molecules in the atmosphere. Very superficial consideration of the real facts will show that such a law will hold only for very small distances near the surface of the medium. The final distribution depends ultimately on the residual electric charge in the particles.<sup>16</sup>

With this effective charge granted we may dispense with the Helmholtz fantastic explanation of mobility and at the same

<sup>13</sup> Lewis, W. C. McC., "System of Physical Chemistry," Vol. I, p. 339 (2nd ed.)

<sup>14</sup> Burton, "Physical Properties of Colloidal Solutions," pp. 86-7 (2nd ed.)

<sup>15</sup> Perrin, "Atoms" (tr. Hammick), Constable, 1916

<sup>16</sup> Burton, *loc. cit.*, pp. 86-9

time simplify Lamb's work on cataphoresis. There must be more than a coincidence in the fact pointed out above, that such a similarity exists between the mobilities of colloidal particles and those of ordinary ions.

Consideration of the mutual action of colloidal particles will introduce an important change in some of the formulae which have been suggested for many colloidal phenomena.

Time and time again we use the constants of the gas equation  $Pv = RT$ . This simple relation is deduced on the supposition of there being no mutual action between the particles (molecules of gas) under consideration. When we introduce such mutual action, we may apply the expression for the virial of the forces; the complete equation may be written.<sup>17</sup>

$$\frac{1}{2} \Sigma m V^2 = \frac{3}{2} pv + \frac{1}{2} \Sigma r F(r)$$

where  $m$  = mass of molecule

$V$  = velocity of molecule

$p$  = pressure of gas

$v$  = volume of gas

$r$  = distance between any two particles

$F(r)$  = law of force acting between two particles.

Putting  $\frac{1}{2} \Sigma m V^2 = RT$  for molecular weight and finding  $p$  we have

$$p = \frac{2}{3} RT \cdot \frac{1}{v} - \frac{1}{2} \cdot \frac{1}{v} \cdot \Sigma r F(r)$$

Wherever the osmotic pressure is treated as a gas pressure, e. g., in formula for Brownian movement, as given by Einstein,<sup>18</sup> and Langevin,<sup>19</sup> or in Perrin's distribution law,<sup>15</sup> the value of  $p$  will involve not only  $RT$  but the expression for the virial

$$\Sigma r F(r)$$

This correction will make Perrin's work agree with experimental results, and will make the Brownian movement depend to a certain extent on the charge on the particle; a particle which is charged and in an atmosphere of charged particles will have a greater Brownian movement velocity than the same particle in an uncharged state. It is on record that when electrolytes are added to a sample of the solution under the ultramicroscope, the Brownian movement is reduced even before coagulation sets in.

<sup>17</sup> Lord Rayleigh, "Scientific Papers," Vol. V, No. 304, p. 238

<sup>18</sup> Einstein, "Untersuchungen Brownsche Bewegung" Ostwald's "Klass. d. Exact. Wiss.," No. 199, Akad. Verlagsges., Leipzig, 1922

<sup>19</sup> Langevin, *Compt. rend.*, 146, 530 (1908)

## SUMMARY

The points considered in the above are the following:

1. Slow rate of fall of small particles.
2. Crystal forces at work in forming the nucleus of colloidal particles.
3. The rôle of surface tension in causing the agglomeration of small particles.
4. The mutual action of colloidal particles due to the possession of an electrical charge.

## DISCUSSION ON E. F. BURTON'S PAPER

### FORCES REGULATING THE SIZE OF COLLOIDAL PARTICLES

T. SVEDBERG: I will not try to go into any detailed discussion of all the interesting points that Professor Burton has presented. I do not want to say much except to make a few scattered remarks. For instance, in regard to the double layer, I do not think that the colloid chemists are now working with the double layer as strictly in the sense of a condenser. For instance, in Gouy's calculations, he assumed that the double layer is diffused in the way Professor Burton suggested. He calculated the thickness of the dielectric in an ordinary condenser that would correspond to a diffused double layer such as spoken of. Gouy found a very interesting result in calculating the thickness of this double layer, *viz.*, that its thickness varied with the concentration of the electrolytes present, under such concentrations as occur actually in ordinary colloid solutions. Of course, we also believe that there is a mutual action between the particles due to electrical action. For instance, Smoluchowski uses the hypothesis that in the case of "rapid coagulation" two particles agglomerate as soon as the centers of the particles come within the radius of a certain sphere of action. We have found that by applying this theory to experimental determinations of rate of coagulation we can measure the radius of action; in most cases this radius of action is exactly equal to the diameter of the particle, that is, the coagulation takes place only when the two particles are in actual contact.

In order that every encounter may lead to agglomeration,

the potential difference across the double layer must be lower than a certain critical value—the so-called “critical potential.” However, coagulation may take place when the potential difference is higher than this critical potential, *i. e.*, the coagulation is said to be “slow.” In this case it is supposed that only a fractional part of the total encounters between particles lead to agglomeration. This shows that the stability of a sol depends in some way upon the charge on the particle. It therefore appears that many colloid chemists already do not operate with the Helmholtz double-layer in its original form.

J. A. WILSON: In the solution surrounding the negative particle portrayed by Dr. Burton, there must be an excess of positive electrical charges over negative charges. In the solution far removed from the surface of the particles, the positive and negative charges must be equal in concentration. But, since the product of the concentrations of positive and negative charges must have the same value everywhere throughout the solution, it is plain that there is a measurable potential difference between the solution wetting the particle and the main body of solution.

I would like to ask Dr. Burton if he does not consider this potential difference to be the active force determining the stability of these particles and not the actual charge itself.

E. F. BURTON: I haven't thought of that at all. I am pretty thoroughly convinced, though, that the distribution of charges outside is such that there is a considerable mutual action between the particles. I have tried the experiment of limiting concentration on silver solution made according to the Bredig method, where the concentration of a common sol was carried out by evaporation in a vacuum. Taking out samples so as to get the concentration at various times gave a curve which showed that the concentration approached a limiting value. This could not be brought about by partial concentration due to impurities in the sol because we measured the mobility and found that it practically did not change at all. So that I do not believe the limiting concentration is brought about by coagulation taking place. The fact that you get different concentrations by different methods might mean that the effect of charges on the particles are different under different circumstances. If you have one particle which

is very highly charged, you would not be able to pack them in so closely as those which haven't such a large charge.

T. SVEDBERG: I am afraid that the apparent limiting concentration obtained by Professor Burton with silver sols is due to dissolved silver salt impurities in the sol as concentration takes place. These impurities would tend to produce partial coagulation of the sol, which would become more apparent. For instance, in certain cases, this "limiting concentration" is not so pronounced. We have produced by means of the centrifuge, a concentration of gold sols which is quite enormous. Running the centrifuge for some minutes causes the gold to settle towards the bottom of the tube in a highly concentrated layer. We actually get a sedimentation equilibrium without coagulation; when the centrifuge is stopped the gold re-diffuses through the liquid.

E. B. SPEAR: I think some years ago it was shown that silver solutions contain both positively and negatively charged particles. In that case it would be very much better to work with platinum. I should like to ask Dr. Burton what his idea is of the mechanism by which the particle becomes charged, is there a transfer of electrons, is there actually a close contact between particles and ions, or is there merely a sphere of influence? I think we have got to have some clear picture of what happens here, because the fact is that if you add electrolytes to sols with electrically charged particles, some of the electrolytic ions go to the bottom, so there must be a pretty close contact if the electrolyte is going to be carried down with the material of the particles.

E. F. BURTON: It is rather hopeless to try to picture what happens, because for this one fact, it is undoubtedly true that ions bearing a charge opposite to that present on the particle, are much more powerful as coagulants, but the ion which bears the same charge does not seem to have any effect at all. Now, it is almost hopeless to try to picture what happens in coagulation; for example, if one adds, say, aluminum sulfate to a silver sol, the aluminum ions produce the coagulation, are probably carried down by the coagulum, but the sulfate ions appear to have no effect at all.

R. A. GORTNER: I have felt the same way that Professor Burton feels, that two particles approaching each other do not



coalesce. For instance, we have two gold particles that will play around together but will not coalesce if we have on the surface of that particle a water film. We have a tremendous surface energy on the small surface and we know how difficult it is to remove water from the surface of a glass vessel. Theoretically, we should have much more activity there. There is certain evidence that this is the case, because when we take a gold sol and precipitate it with a salt we get a rather bulky precipitate. You can filter that off or wash it a few times carefully and you have quite a precipitate. Now if you heat that moist coagulum, all you have left is the merest shimmer of gold in the bottom of the evaporating dish. We have thus dehydrated the precipitate of gold. Now if the precipitated gold carried down that much water, the question in my mind is "how much water does the gold have intimately bound to it when it is in suspension?"

J. A. WILSON: Having given much thought to the problem of coagulation, I think there is a good deal in what Dr. Gortner has said. The difference of potential which I have described is probably the major force operating in preventing the coalescence of the gold particles. It is easy to show how the addition of sodium chloride will lower the measured difference of potential. The charges on the particle come into play only when the surface films wetting two particles merge into one.

R. THIESSEN: I would like to add my observations on carbons. I am working a good deal on all kinds of carbons, and in order to make observations with these, we mix them with linseed oil. Now if one takes a very good carbon black, one that disperses very easily, and the particles are suspended in the linseed oil, they do remain isolated for a length of time, but gradually these particles begin to line up, and they will first form a regular hexagonal net-work. As you watch them, they gradually crawl closer and closer together, and after twelve or twenty-four hours the whole field is aggregated in bunches and keeps on aggregating within certain limits. The different carbon blacks differ largely in that respect. Just what that influence is I would like to know. What makes them line up in this nice net-work? There are other colloidal substances in which the tendency is the same. The tendency is always to coagulate, coalesce. It is very remarkable how they first

line up in a hexagonal net-work and then suddenly tear up the net-work and bunch up.

F. E. BARTELL: In order to get the effect referred to by the last speaker it is necessary to have some volatile component present in the medium. The successive conglomeration of the particles is a result of the gradual evaporation of this component. The particles first seem to collect on the surfaces of small spheres, which on account of the close packing, assume a shape which will give a hexagonal cross-section. This hexagonal net-work is afterwards broken up by an apparent motion of the particles towards the centers of the hexagons, where they pile up into heaps. If one wishes to make a membrane built up on this hexagonal structure, in which ether or alcohol is the volatile component, one would simply immerse the membrane in water at the appropriate stage, in order to remove the volatile substance.

E. B. SPEAR: In regard to that signal phenomenon, if one takes carbon black and dissolves it in a vessel and then evaporates it, one sees a feather-shaped formation, what might be called star-shaped, and the particles of carbon arrange themselves much like the fingers of one's hand.

R. THIESSEN: That is a very common formation with those substances. We run across it many times.

S. E. SHEPPARD: There is one question I would like to ask with regard to the adsorption film of water about a particle. Wouldn't such a film of water effectively change the radius of the particle so that the size would either be incorrect, or, if correct, what evidence is that for the existence or non-existence of the adsorption film?

In the case of small colloidal particles of gold, if the particle rotates about an axis it will have a radius quite different from that of the actual amount of gold but it would simulate a water layer. I want to find out if it is possible to distinguish between those two cases where the mechanical movement of a particle would tend to simulate the water of the film.

E. F. BURTON (COMMUNICATED): With regard to the experiments on the limiting concentration of silver sols, I should like to point out that there was no indication of any increase in impurity such as to cause partial coagulation; the mobility of the particles and the conductivity of the sol remained prac-

tically the same as the concentration proceeded. In considering limiting concentration we have equilibrium, in any case, between the molecular shocks, the electrical repulsion and the force of gravity, which, of course, is constantly acting. In Professor Svedberg's charming experiments with the centrifuge we have the effective force pulling the particles towards the bottom of the dish, which will be several hundred times the force due to gravity and consequently we should expect an entirely new distribution of the particles as the new force tending to cause settling may quite overcome any mutual repulsion between neighboring particles.

Regarding the question submitted by Dr. Wilson as to our view of the seat of the charge on the particle, we must realize that there will be one or more layers of water molecules very closely attached to the particle and it does not appear to be a very crucial point as to whether or not we have the difference of potential between the particle itself and the surrounding water or between this closely adhering layer of water molecules and the surrounding water. I think I should incline to the latter view.

I do not think that the Bredig silver sol can be considered as having both positively and negatively charged particles as suggested by Dr. Spear. Any silver sols having such must be stabilized by some protective colloid. The only drawback in using silver in preference to platinum or gold is the fact that the silver may form the oxide as suggested by Professor Svedberg in this discussion.

The fact that the mobility of colloidal particles and ordinary electrolytic ions are so nearly the same, suggests that there may be a layer of water molecules about both ions and particles, as referred to by Professor Gortner. It might be interesting to experiment on the rate of dehydration of the moist coagulum. One should not trust, however, to impressions obtained by use of the ultramicroscope because one would not be able to differentiate such a water film from the diffraction disc about an isolated particle.

## THE MECHANISM OF THE MUTUAL PRECIPITATION OF HYDROSOLS

BY A. W. THOMAS AND LUCILLE JOHNSON

Among the interesting properties of colloidal substances is the tendency of certain sols to precipitate when mixed, and the apparent indifference of other sols to each other. Linder and Picton<sup>1</sup> stated that the sols that precipitate each other migrate oppositely in an electrical field. Biltz<sup>2</sup> found that the ratio between the amounts of dispersed phases at complete precipitation varies greatly. Billitzer<sup>3</sup> suggested that the equivalence at complete precipitation is electrical, and since that time it has been generally considered that the mutual precipitation is due to neutralization of charges.

Lottermoser<sup>4</sup> suggested that the equivalence may be that of the small amounts of peptizing agents present, and that the precipitation may be due to a chemical action between the peptizing agents, by which they are removed. Data from a few mutual precipitations of silver iodide sol peptized by silver nitrate and silver iodide sol peptized by potassium iodide indicate that the explanation holds for this precipitation. Freundlich and Nathansohn<sup>5</sup> found mutual reaction between sols of like migration in an electrical field, as well as between those of opposite migration.

The purpose of this investigation was the determination of the relation between the amounts of peptizing electrolytes of mutually precipitating sols at the point of maximum precipitation.

The first precipitation studied was that of ferric oxide hydrosol peptized by ferric chloride and silicic acid hydrosol peptized by sodium silicate. The ferric oxide hydrosols were prepared by adding two molar ammonium hydroxide to two molar ferric chloride and purified by dialysis in collodion bags against distilled water.

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<sup>1</sup> Linder and Picton, *J. Chem. Soc.*, **71**, 586 (1897)

<sup>2</sup> Biltz, *Ber.*, **37**, 1095 (1904)

<sup>3</sup> Billitzer, *Z. physik. Chem.*, **51**, 129 (1905)

<sup>4</sup> Lottermoser, *Kolloid-Z.*, **6**, 78 (1910)

<sup>5</sup> Freundlich and Nathansohn, *Kolloid-Z.*, **28**, 258 (1921); **29**, 16 (1921)

The silicic acid sols were prepared by partial neutralization of a solution of water glass by hydrochloric acid. The sols contained the sodium chloride formed in the neutralization. That the sodium chloride was present in insufficient amounts to effect the precipitation was shown by adding to the sol an amount of sodium chloride equal to sixty per cent. of that already present. The precipitating ratios were unchanged.

The experimental work was carried out in the following manner. Varying amounts of one sol were run from a burette into hard glass bacteriological tubes of uniform diameter and clearness, and about 20 cc. in volume. Equal volumes of the other sol were run from a pipette or burette into the tube as quickly and as quietly as possible to avoid mixing. The sols were mixed by inverting the tubes two or three times, with as little agitation as possible, so that the mixing was complete. This was sufficient for mixing if the tubes were not more than three-fourths full and were revolved as they were inverted. The point of maximum precipitation could be clearly seen by successive stages, first the greatest cloudiness in the series, followed by the first separation of particles, and usually the first sediment. The last was frequently over a wider range than the first two stages as the precipitating zone widened rapidly. All observations were made immediately after mixing by holding the series of tubes against a clean or open window. Artificial light was found to be quite unsatisfactory, as was the light late in the afternoon or on a dark day.

Some series precipitated more easily than others, probably because of greater agitation. Vigorous shaking usually precipitated the whole series immediately. A tube of greater diameter than the others or of cloudy or marked glass appeared more cloudy and consequently was misleading. A few series were centrifuged, but the time required in placing them in the centrifuge and the power to throw out the fine particles resulted in complete precipitation over a wide range.

To avoid errors due to an unclean tube or some other factor, three or four determinations were made in each instance.

The sols used were very dilute as the range of precipitation narrowed and sharpened with dilution. To avoid possible differences due to order of mixing the order was always reversed at least once.

The following table gives the results of the experiments:

TABLE I

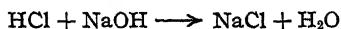
Showing the ratio of ferric chloride expressed in equivalents of hydrochloric acid to sodium silicate expressed in equivalents of sodium hydroxide in the thirty-seven precipitations of ferric oxide sol and silicic acid. The values are milli-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloric acid.

The sols are arranged in the order of their purity, the ratio of sodium silicate in terms of sodium hydroxide to silicon dioxide decreasing from left to right, and the ratio of ferric chloride to ferric oxide decreasing from top to bottom.

Silicic Acid Sols					
Number:	4	2	1	3	5
Mols NaOH/SiO <sub>2</sub> :	1/3.5	1/5.8	1/6.7	1/10.4	1/16.1
Ferric oxide sols					
Mols No. FeCl <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>					
2	1/ 4.8	0.00061	0.00073	0.00080	.....
1	1/ 5.35	0.00080	0.00055	0.00077	.....
3	1/ 5.37	0.00073	0.00069	0.00077	.....
4	1/ 8.65 >100%	0.00096	0.00091	0.00090	.....
15	1/ 9.8	0.00090	0.00100	0.00080	0.00029
6	1/10.6 >100%	0.00106	0.00094	0.00082	.....
17	1/13	0.00101	0.00090	0.00080	0.00043
23	1/14.3	0.00101	0.00091	0.00090	0.00048
21	1/15.9 >100%	0.00098	0.00110	0.00080	0.00044
20	1/18.5	0.00093	0.00100	0.00080	.....
(Excluding)					
2, 1, 3					
Average	>100%	0.00098	0.00095	0.00083	0.00041

This shows that over a wide range of ratios between peptizing agent and dispersed phases of sols, there is a constant ratio between the peptizing agents of mutually precipitating sols and a very varying ratio between the dispersed phases. This leads to the conclusion that the precipitation is due to removal of the peptizing agents by a chemical action between them. As no definite formula can be given for the silicates it is impossible to express the reaction between sodium silicate and ferric chloride in an equation. However, the peptizing ferric chloride and sodium silicate can be given in terms of their hydrolysis products which are in equilibrium with the dispersed phase complex, and consequently in the mutual precipitation of

ferric oxide and silicic acid] sols the reaction may be expressed as:



Another indication of such a reaction is given by the difference of hydrogen ion concentration in the supernatant liquid of precipitation of varying degrees. Varying amounts of silicic acid sols No. 3 (diluted 1:25) were added to 25 cc. of ferric oxide sol No. 4 (diluted 1:10), the precipitate allowed to settle and the hydrogen ion concentration of the supernatant liquid determined with the results given in Table II. The ferric oxide sol is slightly acid, and the silicic acid sol distinctly alkaline to phenolphthalein as indicator.

TABLE II

SHOWING CHANGE IN HYDROGEN ION CONCENTRATION WITH VARYING PRECIPITATION OF FERRIC OXIDE AND SILICIC ACID SOLS

Silicic acid sol. cc.	Precipitation	Negative log hydrogen ion concentration
10	Very slight	
..	Excess of $\text{Fe}_2\text{O}_3$ sol	5.6
16	Maximum pptn.	6.8
18	2nd of series	7.8
20	Slow pptn.	>8.3 (Alkaline to phenolphthalein)

Thus it is evident that maximum precipitation occurs at neutrality as the chemical equivalence of peptizing electrolyte demands and that the acidity increases with excess ferric oxide sol, and the alkalinity increases with excess silicic acid sol.

The ferric oxide sols, excluding Nos. 1, 2 and 3 (which contain the greatest amount of the peptizing agent in proportion to the dispersed phase), give a one to one ratio with silicic acid sols Nos. 1 and 2. With silicic acid sol No. 3, the same ferric oxide sols give a constant ratio with the ferric chloride of the same ferric oxide sols. As the sol becomes "purer" in respect to peptizing agent, it becomes more unstable and the precipitating ratios become more inconstant. This agrees with the general experience with "pure" ferric oxide sols. It is known that when a certain degree of "purity" is passed in a sol, the sol precipitates. The sol containing only a little more than the necessary minimum of peptizing agent is in a metastable condition, and the least disturbance will precipitate it. This

may easily account for the ready precipitation of the pure ferric oxide sols.

Dilution of stable sols does not shift the zone of precipitation appreciably. The effect of diluting unstable sols in mutual precipitation is shown in the following table:

TABLE III

SiO <sub>2</sub> sol	Dilution Fe <sub>2</sub> O <sub>3</sub> sol	Milli-equivalents		NaOH equivalents of HCl equivalents
		NaOH	HCl	
1:50	1:50	0.00057	0.00160	35%
1:100	1:50	0.00069	0.00160	43%
1:200	1:50	0.00080	0.00160	50%

This shows that the amount of peptizing agent in the sol at maximum precipitation increases with dilution. It is possible that this is due to a greater availability of the peptizing agent as suggested—or it may mean that upon greater degree of dilution, the particles are farther apart and there are less chances of collisions, as Kruyt and van der Spek<sup>6</sup> have suggested to explain dilution effects. Greater dilution was impossible as precipitation became almost imperceptible and so slow that it was very difficult to determine the zone of maximum precipitation.

Both ferric oxide and silicic acid sols show erratic results in precipitation, if they contain large amounts of peptizing agent. This is undoubtedly due to the fact that some of the peptizing agent has been absorbed in the coagulum and carried down with it.

Mutual precipitations of the ferric oxide hydrosols and arsenic trisulphide hydrosols peptized by hydrogen sulphide were made. No quantitative data were possible because of the limitations in determining the hydrogen sulfide.

Many attempts were made to drive over the excess hydrogen sulfide and thus determine it directly, but in every instance there was decomposition of the arsenic trisulfide. For example 100 cc. of sol containing only 1% of phosphoric acid (sp. gr. 1.7) was completely dissolved by 15 minutes boiling. This was surprising in view of the generally accepted ideas of the stability of arsenic trisulfide, and may be due to its fine division in the sol. At no time was there precipitation during the heating, unless electrolytes had been added to the point of precipitation.

<sup>6</sup> Kuyt and van der Spek, *Kolloid-Z.*, **25**, 1 (1919)

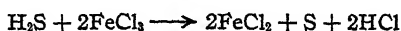


Ward<sup>7</sup> states that at temperatures below 35°C., the hydrogen sulfide can be driven off from arsenic trisulfide without decomposition, but several attempts to remove only the hydrogen sulfide by passing carbon dioxide gas through the pure sol, or the sol precipitated by neutral salts, resulted in appreciable decomposition.

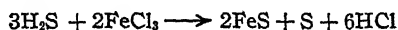
Quantitative determination of the peptizing hydrogen sulfide in a sol by difference between the total sulfur and the sulfur of the arsenic trisulfide was impossible as the amount of hydrogen sulfide present in a sol is so small compared to the arsenic trisulfide that an error of 0.2% in the arsenic or sulphur analysis may easily result in an error of 100% in the determination of the hydrogen sulfide.

An arsenic trisulfide sol was precipitated against a few of the ferric oxide sols, which gave a constant chemical equivalence with silicic acid sols. The peptizing electrolytes were of the same order, but there was too great a variation to draw any definite conclusion. This was not surprising, as any sols studied have given constant ratios only over certain ranges, and this could easily have been out of that range. The determination of a constant precipitating range is only accidental or requires a great number of experiments, and in view of the analytical restrictions it was felt that this did not justify the work required.

If there is an equivalent reaction it would be



With a possibility of



In most precipitations there is no evidence of the latter reaction as the precipitate is yellow. If, however, the sol contains a great amount of the  $\text{H}_2\text{S}$ , there is a blackening which can be explained by the formation of ferrous sulfide.

The most probable ratio would be  $\text{H}_2\text{S}:\text{FeCl}_3:1:2$ . From the calculations with the analysis of the arsenic trisulfide sol, it was more nearly  $\text{H}_2\text{S}:\text{FeCl}_3:2:2$ , an abnormally high value for  $\text{H}_2\text{S}$ . This indicates strongly a high value of the sulfide, due to absorption of impurities by the  $\text{BaSO}_4$ .

<sup>7</sup> Ward, *American Chemist*, 4, 10 (1873)

To test the precipitate for sulfur, 500 cc. of the arsenic trisulfide was precipitated with ferric oxide sol No. 4, the precipitate dried and extracted for five hours with carbon bisulfide. For comparison 500 cc. of the sol was precipitated by aluminium sulfate, the precipitate dried and extracted with carbon bisulfide. Both extractions produced sulfur as was expected from the chance of oxidation of the hydrogen sulfide in the sol, which was an old one, when standing, and of the precipitate during drying. The sol precipitated by the ferric oxide sol yielded about 30% more sulfur than that precipitated by aluminium sulfate. Considering the small amount of hydrogen sulfide present, this difference is an indication that such a reaction had taken place between the ferric chloride and hydrogen sulfide.

It has been generally considered that hydrogen sulfide is the stabilizing agent of arsenic trisulfide sols. In this investigation, it was found that sols that contained an excess of arsenious acid either through decomposing the arsenic trisulfide and driving out some hydrogen sulfide, or by failure to add an equivalent or slight excess of the hydrogen sulfide for the arsenious acid in solution when preparing the sols, were very stable. They gave a sharp range of precipitation with the ferric oxide sols, if sufficiently dilute, and acted in every way as did the arsenic trisulfide sols peptized by hydrogen sulfide. They have the advantage of having a non-volatile peptizing agent, and one that does not oxidize as readily as does hydrogen sulfide, thus being more dependable for quantitative work. The arsenic trisulfide sols peptized by arsenious acid will probably be found more satisfactory for further quantitative work on the mutual precipitation of ferric oxide and arsenic trisulfide sols, than those peptized by hydrogen sulfide have been.

#### CONCLUSIONS

1. It is demonstrated that the precipitating ratios of certain mutually precipitating hydrosols depend upon the peptizing agents.

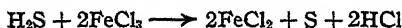
2. There is chemical equivalence between the peptizing agents of ferric oxide hydrosol peptized by ferric chloride, and silicic acid sols peptized by sodium silicate, provided the ratio of peptizing agent to the dispersed phase falls within a

certain range. Outside of this range the precipitation is erratic.

3. Ferric oxide-silicic acid sol precipitations showing chemical equivalence between the peptizing agents at maximum precipitation show little variance in precipitation ratios with dilution, while those showing a divergence from chemical equivalence approach chemical equivalence with dilution.

4. Mutual precipitation of ferric oxide and silicic acid sols is due to the removal of peptizing agents by chemical reactions between them.

5. Qualitative experiment shows that the mutual precipitation of arsenious sulfide hydrosol and ferric oxide hydrosol may be due to the chemical reaction:

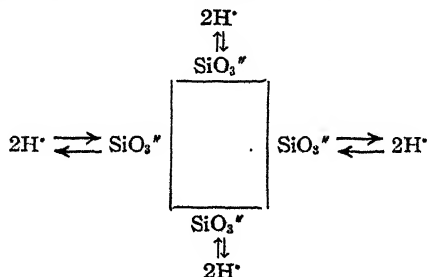


It was impossible to verify this quantitatively due to analytical restrictions.

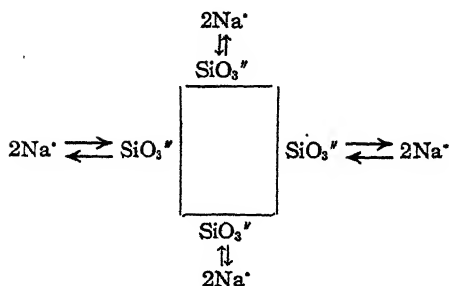
#### DISCUSSION ON THOMAS AND JOHNSON'S PAPER

#### THE MECHANISM OF THE MUTUAL PRECIPITATION OF HYDROSOLS

N. E. GORDON (COMMUNICATED): I am much interested in Dr. Johnson's work on the peptization of silica for a phase of our work on soil colloids at the University of Maryland has led us to similar conclusions *i. e.*, as a result of our work it seems best to assume that the negative charge on silica gel, with respect to water is due to the slight ionization of the silicic acid which the gel forms with the water, thus



Now when this gel is treated with NaOH the charge on the gel becomes more negative due to the formation of sodium silicate



which is more soluble and hence more highly ionized than silicic acid. The sodium ion has a tendency to diffuse to regions of lesser concentration. It cannot do so without carrying the silicate ion in its train, and hence peptization does not occur until the silica particle has been reduced to small enough dimensions to enable the sum of the pulling forces of the sodium ions to drag it to regions of lesser concentration. We have carried out a series of experiments on replacing this sodium with such metals as K, Ca, Mg, Ag, etc., and find all results in harmony with the simple laws of chemical and physical equilibrium. We have also done considerable work on electroendosmosis which confirms our results for the charge on the silica particles, and in conclusion I would say that I believe that Dr. Johnson is quite right in her assumption as far as silica is concerned.

## THE THEORY OF EMULSIFICATION

BY PHILIP FINKLE, HAL D. DRAPER AND JOEL H. HILDEBRAND

To disperse one liquid in another in the form of an emulsion requires the doing of work upon the system equal to the product of the interfacial tension by the increase in surface. An emulsion produced by the mechanical agitation of two pure, incompletely miscible liquids is therefore always unstable, the drops of dispersed liquid coalescing upon contact to decrease the interfacial area. To stabilize an emulsion a suitable third substance must be added. Many very effective emulsifiers are known, but there has been thus far no altogether satisfactory way to predict the relative powers of different emulsifying agents, either to stabilize the emulsions or to determine which of the two liquids shall be dispersed in the other. Some very useful criteria yielded by experience are more in the nature of rules than theories. We will refer to some of these briefly and then proceed to elaborate a hypothesis which seems to account for the behavior of all emulsifying agents for which we have the data to apply it.

To form a stable foam or emulsion requires that the films of enclosing liquid which separate the bubbles or drops, respectively, shall be stable. This cannot be the case with a pure liquid, since a film represents a surface which is far from the minimum possible. It was shown by Rayleigh that a film is stabilized by the addition of some substance which, by virtue of high adsorption at the surface, greatly lowers the surface tension. In such a case the surface tension is larger at a fresh surface than at an old surface, at which there has been time for the adsorption to take place by diffusion, so that if an old surface is threatened with rupture, the new surface thereby formed is stronger than the old, and further strain is diverted from the threatened point. This is the effect of soap in stabilizing the water films between the bubbles in soap suds. Since the globules of dispersed liquid in an emulsion must likewise be held apart by a stable film of the enclosing liquid, the presence of a solute which is highly adsorbed at the interface stabilizes the film and prevents the coalescence of the drops. Thus, soap,

which is adsorbed at a water-oil surface as well as at a water-air surface, stabilizes a water-oil emulsion as it does a water-air "emulsion." The difficulty enters when we consider the difference in the type of the emulsion produced by soaps of the alkali metals on the one hand, which disperses the oil in the water, and heavier metal soaps on the other hand, which disperse the water in the oil, for we have adsorption and lowering of the interfacial tension in both cases, and might expect either an oil or a water film to be stabilized.

Bancroft connects the type of emulsion with the phase which is the best solvent for the emulsifying agent. He says, "If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way, then, to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface."

The idea of a film with two surface tensions, one on the oil side and another on the water side, is rather disconcerting, for no one is likely to measure separately the surface tensions on two sides of an interface, and we have evidence, furthermore, that the emulsifying agent may form films at the interface which are but one molecule thick.<sup>1</sup> The general rule, which this theory implies, that the external phase is the one which is the best solvent for the emulsifier is undoubtedly true in most instances. Thus, the alkali metal soaps are soluble in water and disperse oil in water, while the soaps of iron, zinc, aluminum, etc., which are more soluble in benzene and other solvents of low polarity disperse the water in the other liquid. A contradiction exists, however, in the case of a fatty acid, such as oleic acid, which, though soluble in benzene and not in water, gives an (unstable) emulsion of benzene in water.

<sup>1</sup> N. K. Adams, *Proc. Roy. Soc. Lond.*, **99**, 336 (1921); 101, 452, 516 (1922)

Bhatnagar,<sup>2</sup> on the basis of considerable experimental data, has arrived at what may be regarded as a rule rather than a theory: "All emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil in water emulsions, whilst those having an excess of adsorbed positive ions and wetted by oil give water in oil emulsions."

The rôle played by the orientation of the molecules in the interface in determining the direction of curvature was suggested by Langmuir,<sup>3</sup> who said, "This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.

The size of the colloidal particles is determined by the difference in size between the two ends of the molecules just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed."

Harkins, Davies and Clark<sup>4</sup> have also expressed the opinion that the natural curvature of the film is determined by the orientation of the molecules in the interface. They say, "It seemed to us that the only apparent relation was that to the number of oleate radicals in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore it quite possibly may be the orientation and the form of the molecule together with adsorbed ions in the interface between the dispersoid particles (or small drops), and the dispersion medium which determine the surface energy relations, and therefore the size of the drop at which it becomes stable. In other words, this idea is that the drop would be stable whenever the molecules, together with adsorbed ions, etc., in the interface fit the curvature of the drop. The molecules in the curved surface would not need to be at all of the same kind. If the

<sup>2</sup> Bhatnagar, *J. Chem. Soc.*, **119**, 61, 1760 (1921)

<sup>3</sup> Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916)

<sup>4</sup> Harkins, Davies and Clark, *ibid.*, **39**, 354, 541 (1917)

molecules do not fit in the curved surface, the drop will not be perfectly stable, and will either decrease or increase in size if given time."

It is possible to test the orientation hypothesis in a very striking way in the case of the soaps, where the work of Langmuir<sup>5</sup> and of Harkins<sup>6</sup> justifies the assumption that at an interface between water and some liquid of low polarity, such as benzene, any soap would form an interfacial film, which might be as little as one molecule thick.

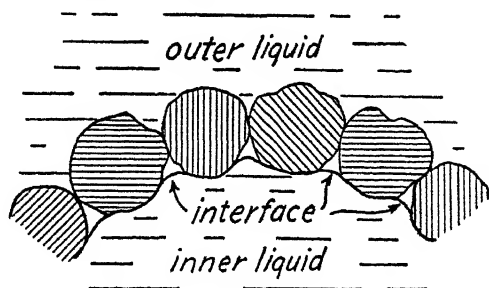


Fig. 1.

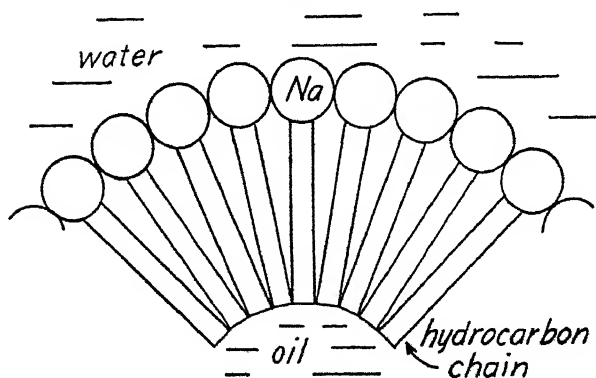


Fig. 2.

Now, if the polar group, in the water, occupies more space than is necessary for the closest packing of the hydro-carbon chain, the latter can be packed more closely if the film is convex on the water side, as illustrated in Fig. 1, in a highly idealized form. It is obvious that the direction and degree of curvature, if this hypothesis is correct, should vary, first, with the atomic

<sup>5</sup> *Loc. cit.*; also *J. Am. Chem. Soc.*, **39**, 1848 (1917).

<sup>6</sup> *Loc. cit.*



volume of the metal, being more convex the larger this volume, and second, with the number of hydrocarbon chains attached to a single metallic atom, according to its valence. Zinc soap, for example, would correspond to Fig. 2, making the interface convex towards the "oil" side; while an aluminum soap should give still more curvature and more stable emulsions of water in oil. Where the cross section of the hydrocarbon chain and of the metallic end are of the same magnitude, there will be no tendency to curvature, and no very stable emulsion, in spite of the high adsorption at the interface, which is still possible.

The relative sizes of the metallic atoms in the various soaps may be inferred from the atomic volumes of the metals, and from their atomic diameters in the free state and in compounds. Values are given in Table I. The atomic diameters are according to Hull,<sup>7</sup> Bragg,<sup>8</sup> and Richards,<sup>9</sup> respectively. Of course, hydration may modify the effective atomic domain, but since, for example, the hydration of silver ion can hardly be as great as that of sodium ion, this factor may be expected to increase rather than to oppose the effect of the differences evident in Table I.

TABLE I  
ATOMIC DIAMETERS IN HALIDES

	Hull	Bragg	Richards	Atomic volumes
Cs	....	4.75	3.8	70.6
K	....	4.15	3.46 (in KCl)	45.3
Na	3.72	3.55	2.85 (in NaCl)	22.9
Ag	2.87	3.55	....	10.3
Ca	3.93	3.40	....	12.6
Mg	3.22	2.85	....	7.0
Zn	2.67	2.65	....	4.6
Al	2.86	2.70	....	3.4
Fe	2.48	2.80	....	2.3

Application of the theory to these figures would indicate that the ability of soaps of Ca, K, Na, Ag to emulsify oil in water would *decrease* in the order given; or, viewed from the other angle, their ability to emulsify water in oil should *increase* in this order; that the soaps of the divalent metals, Ca, Mg, and Zn, should have much *less* ability to emulsify oil in water or

<sup>7</sup> Hull, *Proc. Am. Inst. Elec. Eng.*, **38**, 1171 (1919); *Science*, **52**, 227 (1920)

<sup>8</sup> Bragg, *Phil. Mag.*, [6] **40**, 169 (1920)

<sup>9</sup> T. W. Richards, *J. Am. Chem. Soc.*, **45**, 422 (1923)

much *greater* ability to emulsify water in oil, and further, that they should vary in these respects in the order given.

The soaps of the trivalent metals, Al and Fe, should exhibit the greatest tendency to emulsify water in oil. The values in the several columns for the relative size of Fe and Al atoms do not all agree, so that the relative emulsifying powers are not definitely indicated by these figures. In general, the values for the atomic diameters of the free metals are most reliable, since the values for the atomic diameters in compounds involve two variables which require some further consideration for their determination. On the other hand, there may be doubt that the elementary atom with its electrons occupies the same domain as does the atomic kernel in the compounds. However, there are enough uncertain factors involved to deter us from attempting to make any very fine distinctions on the basis of existing figures for atomic diameters.

To confirm the difference between the volumes of the metallic end of the molecule in Na and Ag soaps we made approximate determinations of the molecular volumes of their stearates as follows:

	In saturated solution in			
	Acetone	Benzene	Methyl alcohol	Average
Na stearate	338	330	...	334
Ag stearate	309	...	291	300

There were known, previous to our own study of this subject, some facts which support this theory of the action of soaps. The soaps of the alkali metals are very effective in stabilizing oil in water emulsions, K soaps being more effective than Na soaps;<sup>10</sup> magnesium soaps emulsify water in oil;<sup>11</sup> salts of the trivalent metals Al and Fe are especially effective in reversing oil in water emulsions stabilized by soaps of the alkali metals.<sup>12</sup> Emulsions of oil in water stabilized by sodium oleate are reversed by adding magnesium, aluminum, ferrous or ferric salts in amounts chemically equivalent to the sodium oleate used.<sup>13</sup>

These facts encouraged us to undertake a more systematic

<sup>10</sup> Neunier and Maury, *Collegium*, 1910, 277; *Chem. Zentr.*, 11, 1416 (1910)

<sup>11</sup> Newman, *J. Phys. Chem.*, 18, 34 (1914)

<sup>12</sup> Bhatnagar, *loc. cit*

<sup>13</sup> Parsons and Wilson, *J. Ind. Eng. Chem.*, 13, 1116 (1921)

study of the applicability of the theory here outlined. Stearates and oleates of the metals listed in Table I were used to prepare several series of emulsions, varying the concentration of soap and the relative amounts of oil and water used, and varying the degree of shaking for the different series, but using equivalent amounts of soaps in any one series. One liquid was always water, the other benzene, xylene or hexane.

Each group of emulsions was placed in a thermostat maintained at 23°C. and the time noted when each emulsion began visibly to break down.

TABLE II

Oleate of	Dispersed phase	Approximate life of emulsion
Cs	benzene	8 weeks
K	benzene	8 weeks
Na	benzene	6 weeks
Ca	water	1 hour
Ag	water	1 day
Mg	water	2 days
Zn	water	2+ days
Al	water	7 days
Fe	water	10 days

Table II gives the results of a typical series. Other series using stearates in place of oleates, and still others using xylene or hexane in place of benzene gave results so entirely in accord with those here given that their detailed reproduction is hardly necessary. The correspondence in all cases was far more closely in accord with the theory than we had dared to anticipate.

The results in these cases are also in accord with the rule that the external phase is the one which is the better solvent for the emulsifier. The soaps of the alkali metals are more soluble in water, the others more soluble in the non-polar liquid. The soaps of Fe and Al have more symmetrical and less polar molecules, and would therefore be expected to dissolve best in solvents of low polarity, while the alkali metal soaps, consisting of a single chain with a highly polar end, cannot dissolve considerably in non-polar liquids, but can, on the other hand, form clusters with the hydrocarbon chains in the interior, which can then dissolve "colloidally" in water.

If the orientation theory is correct, the different degrees of curvature natural to films of different soaps should yield drops

of different sizes. Since the shaking would never produce drops of uniform size in any emulsion, it was necessary to determine

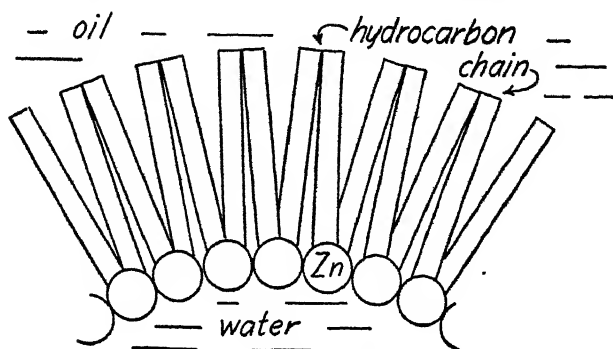


Fig. 3.

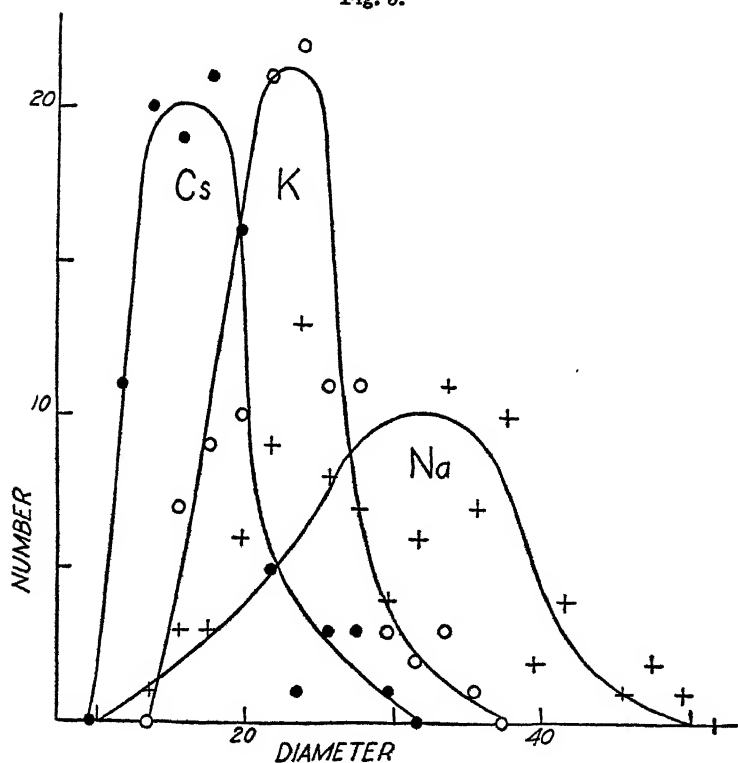


Fig. 4.

the distribution of a large number of drops between different size intervals. (To take the mean size would obviously give

abnormal weight to the occasional very large drops.) A micrometer microscope was used, and the diameter of all drops in the field measured, the field being altered often enough to get a total of 100 drops. The operator did not know which emulsion he was measuring until after he had finished.

Four different series of emulsions with Cs, K and Na stearates were thus measured, the conditions in each series being identical except for the kind of soap used. Table III and Fig. 3 represent the results with one series. The size intervals are represented

TABLE III

Size interval	No. drops		
	Cs soap	K soap	Na soap
9-10	0	0	0
11-12	11	0	0
13-14	20	0	1
15-16	19	7	3
17-18	21	9	3
19-20	16	10	6
21-22	5	21	9
23-24	1	22	13
25-26	3	11	8
27-28	3	11	7
29-30	1	3	4
31-32	0	2	6
33-34	0	3	11
35-36	0	1	7
37-38	0	0	10
39-40	0	0	2
41-42	0	0	4
43-44	0	0	0
45-46	0	0	1
47-48	0	0	2
49-50	0	0	1

in scale divisions of the microscope micrometer, of which 60 div. = 0.01 mm. The other series showed a similar displacement of the maxima, although due to differences in shaking, etc., between the different series, the soap did not yield the same maximum each time.

The flatness of the curve for sodium stearate in Fig. 4 evidently has no significance in view of the relatively small number of drops counted. In the other series no such marked difference occurred.

It is evident from these data that the Ca soap gives the smallest drops and the Na soap the largest, so that the curvatures of the films actually differ in the predicted direction and therefore support the theory.

Many powdered solids have been shown capable of stabilizing emulsions.<sup>14</sup> It seems to be possible to account for the type of emulsion produced by the following hypothesis. It is obvious, first, that the powder must collect at the interface in order to be effective. Now, this will occur only when the solid is wetted by both liquids, with a finite angle of contact of the interface with the solid. In general, one liquid will wet the solid better than the other as represented in Fig. 4, so that the particles will be drawn more largely into the former. If there are enough solid particles to fill the interface the tendency of the interface to contract will cause it to bend, as shown in Fig. 4, in the direction of the more poorly wetting liquid, which makes it easy for the latter to become the enclosed phase. Of course, a solid, in order to behave in this way, must be easily dispersed in the outer liquid, its particles not tending to agglomerate therein or to stick together when serving as protective armour for emulsified drops. One should therefore be able to predict whether or not a given solid powder can stabilize an emulsion, and also which liquid will become the dispersed phase, by noting the angle of contact of the interface with the solid. Data upon this point are not abundant but seem to be altogether confirmatory, and a microscopic examination of an emulsion of water in benzene stabilized by lamp-black confirmed the picture given in Fig. 4.

We suggest that this picture may serve to explain the Bancroft rule that a colloidal emulsifier causes the phase in which it is soluble to be external. A colloidal particle with only a few polar groups upon it would remain largely in the oil phase and *vice versa*, so that the natural curvature of the surface may be determined in much the same way as with powdered emulsifiers.

#### SUMMARY

1. The present status of the theory of emulsification has been outlined.

<sup>14</sup> Cf. Pickering, *J. Chem. Soc.*, **91**, 2010 (1907); *Kolloid-Z.*, **7**, 11 (1910). Sheppard, *J. Phys. Chem.*, **23**, 634 (1919). Schlaepfer, *J. Chem. Soc.*, **113**, 522 (1918). Moore, *J. Am. Chem. Soc.*, **41**, 940 (1919).

2. The types and relative stabilities of emulsions formed by the aid of various soaps have been explained by the aid of the theory of orientation of the soap molecules in the interface.

3. The curvature of the film of soap adsorbed at the interface is more convex towards the water, yielding more stable emulsions of the oil-enclosed type, the larger the metal atom in the soap.

4. As the number of hydrocarbon chains attached to a single metallic atom increases (with the valence of the metal) the curvature is reversed, becoming strongly convex towards the oil phase with soaps of the trivalent metals, Al and Fe, which yield the most stable emulsions of water in oil.

5. Experimental data upon the type and relative stabilities of emulsions of various liquids with water show that the transition from the most stable oil-enclosed to the most stable water-enclosed emulsion for both stearates and oleates follows the order: Cs, K, Na, Ca, Ag, Mg, Zn, Al, Fe. This order is in accord with the valences and atomic diameters of the metals, as interpreted by the orientation theory.

6. It is suggested that the type of emulsion produced by a solid powder is determined by the angle of contact of the interface with the solid. In order for the powder to remain in the interface the angle must be finite; and unless the angle is  $90^\circ$ , the interface will be on one side or the other of the points of contact of the particles, and its tension will cause the film to be concave on that side.

DISCUSSION ON THE PAPER BY PHILIP FINKLE, H. D. DRAPER  
AND JOEL HILDEBRAND

THE THEORY OF EMULSIFICATION

L. KAHLBERG: I would like to ask what evidence there is of these concrete shapes of molecules, or do I understand that you didn't want to shape these molecules that way.

P. FINKLE: That is simply a diagrammatical way of expressing it.

L. KAHLBERG: There is no experimental evidence attached to that.

P. FINKLE: No.

E. K. CARVER: I think the speaker is quite right in that all

old theories are more or less generalizations instead of explanations. It seems to me that another explanation which works in this case about as well as the one advanced is that these particles of the soap act as an armor plate around the globules, preventing cohesion. When the emulsion is made the drops that are not protected immediately coalesce. Last fall a student of mine made a solution of a fatty acid of three carboxyl radicals trying to get a fatty radical which would have a larger volume than the sodium in an attempt to prove this same theory, but contrary to expectations the opposite results were obtained, that is, it didn't seem to be the size of the fatty acid which determined it, but the solubility.

P. FINKLE: Oleic and stearic acids are both soluble in benzene and not in water, yet neither of them yields a water in oil emulsion, but quite the reverse. So I think that disposes of the idea that it depends upon what phase the emulsifying agent is soluble in. Regarding the armor plate, of course that is an old idea, but it does not explain why with certain emulsifying agents you will get oil in water emulsions and with some others water in oil.

J. ALEXANDER: I think Dr. Hildebrand and Dr. Finkle are to be congratulated for giving us some idea of why it is that some of these compounds are so wet and others are so dry. They have explained, however, how, with the inter-phase curvature, it is that the one goes towards the aqueous phase and the other does not.

W. V. EVANS: I would like to ask Dr. Finkle if he has made any experiments with smaller molecules, such as sodium chloride.

P. FINKLE: Those salts do not act as emulsifying agents. The molecules of emulsifying agents are orientated in a definite way, but we must not lose sight of the fact that where you have very small molecules, undoubtedly the thermal agitation would tend to disrupt this tendency, whereas in the case of larger molecules they are not affected by the thermal agitation.

W. A. GIBBONS: I should like to ask if this theory will possibly be extended to indicate what substances will act as emulsifying substances. As I remember it, in soap you have to have eight or nine carbon atoms in a chain before you get this effect. I do not quite see how that explains the conditions arising in this substance, but perhaps it does.



P. FINKLE: I thought I brought the point out, that if you have very small molecules they undoubtedly will be affected by the thermal agitation at the interface, whereas if you have larger molecules, they will withstand these forces. I think that perhaps is the reason why larger molecules do act as emulsifying agents, that is, they are not displaced from the positions they assume, as smaller molecules would be.

W. A. GIBBONS: I would like to ask if any experiments have been carried out in which you used molecules with more than one polar group and with solutions in which the molecule would be tipped. As it seems to me, the difference between these various soaps would be minimized under those conditions. You could not distinguish between a potassium or a sodium soap if you had the organic molecule tilted in such a way as has been proposed by Harkins, so that the actual amount of space cross-section per molecule would be very much larger than where you have a molecule standing perfectly erect.

P. FINKLE: This question of whether the molecule stands perfectly erect or whether it stands in a spiral arrangement I do not think has been definitely settled. Now, suppose we grant that this portion of the molecule is tilted. When you have crowding of these molecules, isn't it reasonable to assume that those differences would be made up by an arrangement of these carbon chains in such a way that they will be packed closely together and be forced, as it were, to stand erect, as this diagram represents?

L. S. PALMER: I have been looking for some time for a theory of emulsification which would explain the fact that you can take an emulsion of fat in cream and agitate it to change that emulsion to an emulsion of water in fat, which you do when you change cream into butter. Of course everyone knows that cream is an emulsion of the oil in water type. Butter is also a very fine emulsification, of water in oil type. Yet, through agitation, without any change apparently of the materials surrounding it, you change from one type of emulsion to another. Those of us who are familiar with emulsion theories are familiar with the results of Clowes.

P. FINKLE: All I can say is that we are certainly dealing with two entirely different systems in dealing with a simple system of water in oil and an emulsifying agent, and the very com-

plex system, milk. In the latter there are many substances whose chemical nature we do not understand—the complex proteins, and also salts. Before attempting to explain why agitation brings about a change from one type of emulsion to the other it is necessary that the problems connected with the chemical composition of milk be elucidated.

H. C. DEMING: It seems to me that there probably is orientation in a molecule, but I believe the investigator is rather unfortunate in using for experimental data results that could be explained just as well by solution. Have any investigators done any work on other systems that could not be explained by the solution theory?

P. FINKLE: I think I mentioned twice the fact that oleic acid and stearic acid are insoluble in water but are soluble in benzene. Therefore, according to the solution theory you should get, by using these acids—as emulsifying agents, emulsions of water in oil. Well, you don't get that, you get an emulsion of oil in water.

H. C. DEMING: How do you explain that?

P. FINKLE: Why explain it, except on the basis of our theory?

H. C. DEMING: You explained it in the case of the salts.

P. FINKLE: We don't know what the relative size of the carboxyl portion of the molecule is as compared with the hydrocarbon chain. However, the volume of this must be larger than the volume of the hydrocarbon chain, since the emulsion is the oil in water type. You certainly cannot explain it on the so-called solubility theory.

## THE SWELLING OF PROTEIN JELLIES

BY JOHN ARTHUR WILSON

The purpose of this paper is to present a quantitative theory of the swelling of protein jellies that throws much light upon the fundamental mechanism of many industrial and biological processes and, indeed, upon colloidal behavior in general. The investigations culminating in this theory were begun by Professor H. R. Procter<sup>1</sup> in 1897. While attempting to arrive at a rational explanation of the molecular mechanism of tanning, he was continually confronted by the necessity of first explaining the mechanism of swelling. Quantitative development of the theory of swelling, however, had to await the appearance of Donnan's<sup>2</sup> theory of membrane equilibria, which was applied by Procter<sup>3</sup> to the swelling of gelatin and further developed by Procter and Wilson<sup>4</sup> into a quantitative theory of the swelling of protein jellies. In an extensive series of researches, Loeb<sup>5</sup> has extended this work to include also the osmotic pressure, viscosity, stability, and electrical potential differences of protein systems as well as a general theory of colloidal behavior.

Instead of tracing the development of the theory of swelling from Procter's earliest work to its present status, it will simplify matters to present the theory from the deductive reasoning furnished later by Wilson and Wilson.<sup>6</sup> They set out to prove that the entire equilibria can be determined quantitatively from the orthodox laws of physical chemistry on the simple assumption that gelatin, or any protein, combines with hydrochloric acid to form a highly ionizable chloride. It seemed that success in this would furnish substantial proof of the correctness of the theory.

<sup>1</sup> Cf. "Action of Dilute Acids and Salt Solutions upon Gelatin," H. R. Procter, *Kolloidchem. Behefte*, 1911; *J. Am. Leather Chem. Assoc.*, 6, 270 (1911)

<sup>2</sup> F. G. Donnan, *Z. Elektrochem.*, 17, 572 (1911)

<sup>3</sup> "Equilibrium of Dilute HCl and Gelatin," H. R. Procter, *J. Chem. Soc.*, 105, 313 (1914)

<sup>4</sup> "Acid-Gelatin Equilibrium," H. R. Procter and J. A. Wilson, *J. Chem. Soc.*, 109, 307 (1916)

<sup>5</sup> "Proteins and the Theory of Colloidal Behavior," Jacques Loeb, McGraw-Hill Book Co., New York, 1922

<sup>6</sup> "Colloidal Phenomena and the Adsorption Formula," J. A. and W. H. Wilson, *J. Am. Chem. Soc.*, 40, 886 (1918)

## THE ACID-PROTEIN EQUILIBRIUM

In order to make the reasoning general, let us consider the hypothetical protein G, which is a jelly insoluble in water, is completely permeable to water and all dissolved ionogens considered, is elastic and under all conditions under consideration follows Hooke's law, and combines chemically with the hydrogen ion, but not the anion, of the acid HA according to the equation

$$[G] \times [H^+] = K[GH^+] \quad (1)$$

In other words, the compound GHA is completely ionized into  $GH^+$  and  $A^-$ . (The brackets indicate concentration in mols per liter.)

Now take a strip of the jelly equal to one millimol of G and immerse it in an aqueous solution of HA. The acid diffuses into the jelly where some of the hydrogen ions are removed from solution by combining with the protein, leaving the absorbed solution more concentrated in the anion  $A^-$  than in hydrogen ion. Each hydrogen ion combining with the protein adds one positive electrical charge to the insoluble mass which is balanced by one anion in the absorbed solution. Although  $[A^-]$  must be greater than  $[H^+]$  in the absorbed solution,  $[H^+]$  and  $[A^-]$  are necessarily equal in value in the external solution and this unequal distribution of ions between the absorbed and external solutions causes them to be separated into two phases.

When equilibrium has been established between the two phases, let

$$x = [H^+] = [A^-]$$

in the external solution. In the jelly phase let

$$y = [H^+],$$

and

$$z = [A^-]$$

balanced by positive charges on the protein

whence

$$[A^-] = y + z$$

Following Donnan's line of thermodynamic reasoning, we can calculate the relation of the variables  $x$ ,  $y$ , and  $z$  at equilibrium. If a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged; that is, no work will be done. The change here considered is the

transfer of  $\underline{dn}$  mols of  $H^+$  and  $A'$  from the external solution to the jelly phase. The work, which equals zero, is

$$\underline{dn}.RT.\log \frac{[H^+]_s}{[H^+]_j} + \underline{dn}.RT.\log \frac{[A']_s}{[A']_j} = 0,$$

where  $s$  indicates concentrations in the external solution and  $j$  those in the jelly phase, and hence

$$[H^+]_s \times [A']_s \times [H^+]_j \times [A']_j$$

or

$$x^2 = y(y + z) \quad (2)$$

Equilibrium will be established only when the product of the concentrations of  $H^+$  and  $A'$  has the same value in both the external solution and the jelly phase.

Because this equation of products is of vital importance to the theory, any doubt as to its validity should be dispelled at the outset. The derivation of the equation need not involve the use of thermodynamics, since it can readily be visualized. In passing from one phase to the other, the oppositely charged ions must move in pairs, since they would otherwise set up powerful electrostatic forces that would prevent their free diffusion. For this reason a cation or anion striking the interface alone could not pass through into the other phase, but there is nothing to prevent the passage from one phase to the other of anions and cations striking the interface together in equivalent numbers. The rate of transfer of these ions from one phase to the other thus depends upon the frequency with which they chance to strike the interface in pairs, which is obviously measured by the product of their concentrations. At equilibrium, the rate of transfer of  $H^+$  and  $A'$  from the external solution to the jelly exactly equals the rate of transfer of these ions from the jelly to the external solution, from which it follows that the product of the concentrations of these ions has the same value in both phases.

Given Equation 2, the rest is simple. Here we have the product of equals equated to the product of unequals, from which it is apparent, mathematically, that the sum of the unequals is greater than the sum of the equals, or that

$$2y + z > 2x$$

The reasoning thus indicates that the sum of the concentrations of  $H^+$  and  $A'$  is greater in the jelly than in the external solution,

at equilibrium. If we represent the excess concentration of the jelly over the external solution by  $e$ , then

$$2y + z = 2x + e, \quad (3)$$

or (from (2) and (3))

$$x = y + \sqrt{ey}$$

which shows us further that  $x$  is greater than  $y$ , or that the hydrogen ion concentration is greater in the external solution than in the jelly. This, in turn, shows that  $[A']$  is greater in the jelly than in the external solution.

Since  $[A']$  is greater in the jelly than in the surrounding solution, the anions of the protein compound will tend to diffuse outward into the external solution, but this they cannot do without dragging their protein cations with them. These protein cations, however, are not in solution in the generally accepted sense, but form part of an elastic structure which resists the pull of the anions, which are in solution. The quantitative measure of this outward pull is obviously represented by the value  $e$  and, according to Hooke's law

$$e = CV, \quad (4)$$

where  $C$  is a constant corresponding to the bulk modulus of the protein and  $V$  is the increase in volume, in cubic centimeters, of 1 millimol of the protein.

Since we have taken 1 millimol of G,

$$[G] + [GH^+] = 1/(V + a)$$

or

$$[G] = 1/(V + a) - z, \quad (5)$$

where  $a$  is the initial volume of 1 millimol of the protein. From (1) and (5),

$$z = y/(V + a) (K + y), \quad (6)$$

and from (2) and (3),

$$z = e + 2\sqrt{ey}. \quad (7)$$

From (4) and (7),

$$z = CV + 2\sqrt{Cey}, \quad (8)$$

and from (6) and (8),

$$(V + a) (K + y) (CV + 2\sqrt{Cey}) - y = 0, \quad (9)$$

where the only variables are  $V$  and  $y$ .

If the molecules or atoms of the protein are not themselves permeable to all ions considered, the quantity  $a$  should not be taken as the whole of the initial volume of the jelly, but only as the free space within the original, dry jelly through which ions can pass. For our hypothetical protein, then, we shall consider the limiting case where the value of  $a$  is zero. This assumption in the case of gelatin introduces errors less than the probable experimental error because of the relatively large values for  $V$  over the significant swelling range. Equation 9 thus reduces to

$$V(K + y)(CV + 2CVy) - y = 0. \quad (10)$$

Knowing the values of the constants,  $K$  and  $C$ , we can plot the entire equilibrium as a function of any one variable; given  $y$ , we can calculate  $V$  from (10); given  $V$  we can calculate  $e$  from (4); given  $y$  and  $e$ , we get  $z$  from (7); and we can then get  $x$  from (3).

Procter and Wilson obtained the value  $K = 0.00015$  for the sample of gelatin used in their experiments by adding successive portions of standard HCl to a dilute solution of the gelatin and noting the corresponding changes in  $p_H$  value by means of the hydrogen electrode. The difference between the concentration of hydrogen ion that would have been found upon adding the acid to pure water and that actually found by adding it to the same volume of gelatin solution was taken as the amount of acid combined with the gelatin, or as the value of  $[GH^*]$  in Equation 1. Substituting any two sets of determinations of  $[GH^*]$  and  $[H^*]$  in Equation 1 and solving the resulting equations simultaneously, the value of  $K$  can be found. It is significant that the value of  $K$  was determined for gelatin in solution and independently of swelling experiments.

This left only one constant to be determined from the swelling experiments themselves.  $C$  was found by substituting experimental values for  $V$  and  $e$  in Equation 4. It was found to vary with the temperature and with the quality of the gelatin, as would have been expected, but had the value 0.0003 for the sample of gelatin used by Procter and at 18°C., the temperature of his experiments.

In order to compare calculated values for  $V$  with experimental determinations of the increase in volume of 1 gram of gelatin, it

is necessary to know its equivalent weight. Procter originally regarded gelatin as a diacid base with a molecular weight of 839, but later work by Procter and Wilson showed that it should rather be regarded as acting as a monacid base, with an equivalent weight of 768, in acid solutions not sufficiently concentrated to cause decomposition. They found that 768 grams of gelatin combine with a limiting value of 1 mol of hydrochloric acid and the combination resembles that of HCl with a weak, monacid base. For this reason we may use the value 768 as the equivalent weight of gelatin. As for the molecular weight of gelatin, no convincing figures have yet been produced and it may be questioned whether they would have any real value, if obtained. We look upon a plate of gelatin as a continuous network of chains of amino acids, there being no individual molecules, unless one wishes to look upon the entire plate of gelatin as one huge molecule.

By substituting the values for  $K$  and  $C$  in Equation 10, Wilson and Wilson were able to calculate all of the variables of the equilibrium for gelatin and HCl over the range covered by Procter's experiments.

Procter's general method of experimentation was briefly as follows: Sheets of thin, purified bone gelatin were cut into portions containing exactly 1 gram each of dry gelatin. One portion was put into each of a series of stoppered bottles containing 100 cubic centimeters of HCl of definite concentration. After 48 hours, which was shown to be sufficient for the attainment of practical equilibrium, the remaining solution was drained off and titrated with standard alkali. The gelatin plates were quickly weighed and the volume of solution absorbed was calculated from the increase in weight of the plates. The swollen gelatin was then put back into the bottles and covered with enough dry sodium chloride to saturate the solution which had been absorbed by the gelatin. This caused the gelatin to contract and give up the absorbed solution. After 24 hours, when equilibrium was again established, the solution expelled by the salt was drained off and titrated to determine the amount of free acid which had been absorbed by the gelatin. A small amount, usually about 1 cubic centimeter, of solution always remained unexpelled by the salt and, although not strictly true, this was assumed to have the same concentration



of free acid as the portion expelled, due allowance being made for the increase in volume of solution due to saturating it with salt. The acid still unaccounted for was assumed to be combined with the gelatin base.

A set of checks was obtained by dissolving the gelatin, after saturating with salt, in warm water and titrating with standard alkali, using both methyl orange and phenolphthalein, the former indicating the free acid left in the jelly and the latter the total, including the acid combined with the gelatin base, which was obtained by difference.

TABLE I  
AT EQUILIBRIUM

Initial [HCl]	[HCl] in soln.	V calcu- lated	Cc. solution ab- sorbed by 1 g. gelatin		[HCl] in jelly		[Total chloride in jelly]	
			Calcu- lated	Ob- served	Calcu- lated	Ob- served	Calcu- lated	Ob- served
0.006	0.0011	33.3	43.4	44.1	0.0001	0.0005	0.012	0.014
0.008	0.0018	37.5	48.8	48.7	0.0002	0.0004	0.014	0.015
0.010	0.0025	41.7	54.3	59.9	0.0004	0.0004	0.016	0.015
0.010	0.0028	42.7	55.6	58.4	0.0004	0.0004	0.017	0.015
0.010	0.0032	43.2	56.2	53.7	0.0005	0.0005	0.019	0.017
0.015	0.0073	40.8	53.1	57.9	0.002	0.002	0.024	0.020
0.015	0.0077	40.2	52.3	52.2	0.002	0.002	0.025	0.022
0.015	0.0120	37.5	48.8	51.9	0.005	0.006	0.031	0.027
0.020	0.0122	37.3	48.6	51.7	0.005	0.006	0.031	0.027
0.025	0.0170	34.5	44.9	40.4	0.008	0.009	0.036	0.037
0.025	0.0172	34.3	44.7	48.1	0.008	0.009	0.036	0.031
0.050	0.0406	26.7	34.8	36.4	0.026	0.030	0.063	0.061
0.050	0.0420	26.4	34.4	31.1	0.027	0.030	0.065	0.068
.....	0.0576	24.0	31.2	34.0	0.041	0.043	0.082	0.079
0.075	0.0666	23.0	29.9	27.9	0.049	0.050	0.092	0.095
0.075	0.0680	22.8	29.7	29.1	0.050	0.053	0.094	0.092
0.100	0.0930	20.7	27.0	23.1	0.072	0.072	0.121	0.126
0.100	0.0944	20.5	26.7	26.4	0.073	0.072	0.122	0.121
.....	0.1052	19.8	25.8	29.8	0.083	0.085	0.134	0.128
0.125	0.1180	18.9	24.6	24.4	0.095	0.090	0.148	0.148
0.150	0.1434	17.9	23.3	24.0	0.118	0.118	0.174	0.173
0.150	0.1435	17.9	23.3	24.2	0.118	0.118	0.174	0.172
0.175	0.1685	17.1	22.3	23.5	0.141	0.138	0.200	0.200
0.200	0.1925	16.3	21.2	20.6	0.164	0.161	0.225	0.229
0.200	0.1940	16.2	21.1	22.7	0.166	0.165	0.227	0.225
0.200	0.1945	16.2	21.1	22.1	0.167	0.164	0.228	0.226
0.250	0.2450	15.1	19.7	20.2	0.213	0.210	0.279	0.281
0.300	0.2950	14.0	18.2	20.0	0.261	0.260	0.332	0.332

In Table I and in Figs. 1 and 2 are given Procter's experimental values for the volume of solution absorbed by 1 gram of gelatin, the free acid left in the external solution at equilibrium,

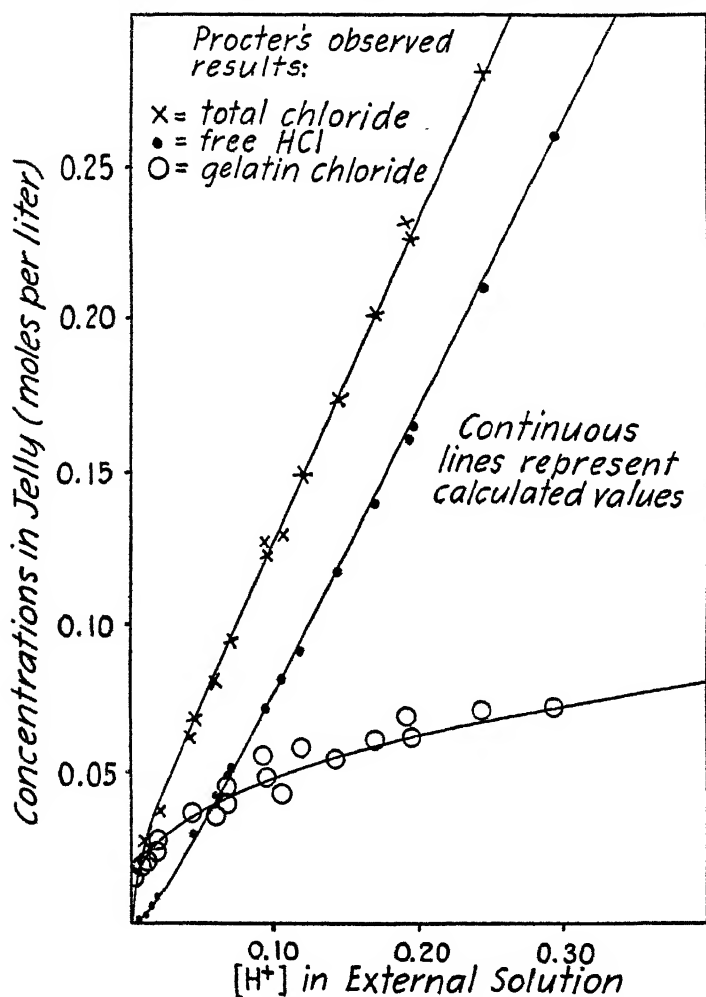


Fig. 1.—Observed and calculated values for the distribution of HCl in the system gelatin-HCl-water.

the free acid in the jelly, and the acid combined with the gelatin base. These were taken from the table on page 317 of Procter's paper, "The Equilibrium of Dilute Hydrochloric Acid and

different values for the constants,  $K$  and  $C$ , as well as for equivalent weight. It is interesting to reason from the theory what differences in swelling would result from changes in the values of the constants. Since  $V = e/C$ , an increase in the value of  $C$  means a corresponding decrease in the degree of swelling. The effect of a change in the value of  $K$ , the hydrolysis constant of the protein, is shown in Fig. 3 for a fixed value of  $C$ . At  $K = 0$ , the point of maximum swelling occurs at  $x = 0$  and has the value  $1/\sqrt{C}$ . As  $K$  increases in value, the point of maximum swelling decreases in value and occurs at increasing values for  $x$ . At  $K = \infty$ , the point of maximum has the value zero and occurs at  $x = \infty$ .

According to the theory, all monobasic acids should produce the same degree of swelling of gelatin for any fixed hydrogen ion concentration, under constant conditions, provided the gelatin salts formed are ionized to the same extent. It was formerly thought that different monobasic acids produce different degrees of swelling, following the order known as the Hofmeister series of the ions, but Loeb showed that earlier investigators, through failure to measure the hydrogen ion concentration, had fallen into the error of attributing to the several acids effects caused merely by differences in hydrogen ion concentration. He found, at a fixed value for  $x$ , that practically the same degree of swelling is produced by all monobasic acids, as well as such acids as phosphoric and oxalic at concentrations at which they act as monobasic.<sup>8</sup>

The calculation of the degree of swelling of proteins in solutions of polybasic acids is not quite so simple as for monobasic acids. Suppose that G were to combine with the hydrogen ion, but not the anion, of the polybasic acid  $H_aA$ . Letting  $x$  represent the concentration of the polyvalent anion in the external solution at equilibrium,  $z$  the concentration of the anion of the gelatin salt, and  $y + z$  the total concentration of anion in the jelly, it is evident from the Donnan theory that

$$x^{a+1} = y^a(y + z)$$

and, by inspection of this equation, we see that

$$(a + 1)x < (a + 1)y + z,$$

<sup>8</sup> Compare "Valency Rule and Alleged Hofmeister Series in the Colloidal Behavior of Proteins," Jacques Loeb and M. Kunitz, *J. General Physiol.*, **5**, 665-707 (1923)

or that

$$(a + 1)x + e = (a + 1)y + z.$$

The total concentration of diffusable ions is greater in the jelly than in the external solution by the amount  $e$  and swelling in degree directly proportional to  $e$  will result. It can readily be seen that as  $x$  increases from zero, without limit,  $e$  and the degree of swelling increase to a maximum and then decrease, approaching zero, for  $z$  has a limiting value since it cannot exceed the total concentration of gelatin. At  $x = 0$ ,  $y = 0$ , and  $e = 0$ . As  $x$  increases without limit, our equations approach the limiting relations

$$xa+1 = ya+1$$

and

$$(a + 1)x + e = (a + 1)y,$$

from which it is evident that  $x = y$  and  $e = 0$ .

The extent of swelling by polybasic acids, which combine as such with the protein, will be considerably less than that caused by monobasic acids, as Loeb has shown, because fewer anions will be associated with equivalent weights of the protein. For example, for equivalent weights of gelatin sulfate and gelatin chloride, there would be only half as many sulfate ions as chloride ions. For very small values of  $x$ , we should therefore expect sulfuric acid to produce only half as much swelling as hydrochloric acid at the same hydrogen ion concentration and this is actually the case.

#### REPRESSION OF SWELLING BY SALTS

The theory accounts quantitatively for the action of neutral salts in repressing the swelling of proteins by acid. In the system described above, in which the protein G was immersed in a solution of HA, consider the addition of the mono-monovalent salt MN, neither of whose ions combine with G. At equilibrium, let the concentration of  $M^+$  be represented by  $u$  in the external solution and by  $v$  in the jelly. It is evident from the general equation of products that the product

$$([H^+] + [M^+]) \times ([A^-] + [N^-])$$

will have the same value both in the external solution and in the solution absorbed by the protein, or that

$$(x + u)^2 = (y + v)(y + v + z),$$

from which

$$e = 2(y + v) + z - 2(x + u).$$

Solving the two preceding equations simultaneously and substituting  $CV$  for  $e$ , we get

$$CV = -2(x + u) + \sqrt{4(x + u)^2 + z^2}.$$

Now, if the value of  $x + u$  increases while  $z$  remains constant, the value of  $V$  will decrease. The addition of  $MN$  to the system increases  $u$  and hence must cause a decrease in the degree of swelling, since it increases  $z$  only by causing a diminution of the volume of the jelly.

It is important to recognize that the repression of swelling by salts does not depend upon any repression of ionization of the protein salt. The added salt acts so as to lower the value of  $e$ , the measure of the degree of swelling, by bringing about a change in the distribution of ions between the jelly and the external solution. Any repression of ionization of the protein salt would necessarily assist in repressing the swelling, but in the case of gelatin chloride the swelling is markedly repressed long before there is any appreciable repression of ionization of the gelatin chloride measurable by means of either calomel or silver-chloride electrodes.<sup>9</sup>

#### THE ALKALI-PROTEIN EQUILIBRIUM

Proteins are amphoteric substances, reacting both as weak acids and as weak bases. In this respect, they retain the properties of the amino acids from which they are formed. Hydrated aminoacetic acid is capable of assuming either a positive or negative charge, or both, by ionizing as acid or base, or both, thus:  $H^+ + 'OOC.CH_2.NH_2.HOH = HOOC.CH_2.NH_2.HOH = HOOC.CH_2.NH_2.H^+ + OH'$ . The ionization constant of a protein as an acid may be represented as follows:

$$[H^+] \times [G'] = K_a[GH]$$

But

$$[H^+] \times [OH'] = K_w, \text{ or } [H^+] = K_w/[OH'],$$

from which

<sup>9</sup> See "Ionization of Protein Chlorides," David I. Hitchcock, *J. General Physiol.* 5, 383-94 (1923)

$$[\text{GH}] \times [\text{OH}'] = k[\text{G}'], \text{ where } k = K_w/K_a.$$

But this is essentially the same as equation (1) except for the fact that  $[\text{H}^+]$  is replaced by  $[\text{OH}']$ . It is thus apparent that proteins will behave in solutions of increasing concentration of alkali much as they do in solutions of increasing concentrations of acid, so long as they undergo no chemical change other than that of salt formation. Actually maximum swelling of gelatin occurs in acid solution at a concentration of about 0.004 mol of hydrogen ion per liter and in alkaline solution at a concentration of about 0.004 mol per liter of hydroxide ion. The effect of valency is similar in both acid and alkaline solutions. Loeb found that the diacid bases calcium and barium hydroxides give points of maximum swelling for gelatin only half as great as given by monacid bases. For a given  $p_{\text{H}}$  value, the amount of swelling is determined by the valency of the ions of opposite sign to that of the protein ions rather than by the specific nature of the ions themselves.

There is reason to believe, however, that gelatin, and some other proteins undergo a change of form in passing from acid to alkaline solution, the form stable in alkaline solution showing a marked tendency to pass into solution. Wilson and Gallun<sup>10</sup> found two points of minimum swelling of collagen as a function of  $p_{\text{H}}$  value, one at 5.1 and the other at 7.6. Later Wilson and Kern<sup>11</sup> showed that gelatin also has two points of minimum swelling, one at  $p_{\text{H}} = 4.7$ , the generally accepted isoelectric point of gelatin, and the other at 7.7. Following this, Parker Higley,<sup>12</sup> at the University of Wisconsin, investigated the absorption spectra of gelatin dispersions of different  $p_{\text{H}}$  value and plotted a series of curves, at several densities, for the wave length of maximum absorption in the ultraviolet as a function of  $p_{\text{H}}$  value. The curves all show two points of minimum, one at  $p_{\text{H}} = 4.68$  and the other at 7.66, coinciding with the points of minimum swelling of gelatin. Discussion of the nature of the change of form of proteins in passing from acid to alkaline solution may well be left until more data are available.

<sup>10</sup> "The Points of Minimum Plumping of Calf Skin," John Arthur Wilson and Albert F. Gallun, Jr., *J. Ind. Eng. Chem.*, **15**, 71-2 (1923)

<sup>11</sup> "The Two Forms of Gelatin and Their Isoelectric Points," John Arthur Wilson and Erwin J. Kern, *J. Am. Chem. Soc.*, **44**, 2633 (1922)

<sup>12</sup> Advance note

## STRUCTURE OF GELATIN JELLIES

Procter's<sup>13</sup> investigations of the behavior of gelatin jellies led him to regard them as having a structure consisting of a network of molecules cohering to each other, but leaving interstices large enough to permit the passage of water and simple molecules and ions. The long chains of amino acids making up the protein molecules are peculiarly fitted to produce such a structure through combination of the acid and basic terminals of these chains. A hot solution of gelatin may be looked upon as a true solution consisting of individual gelatin molecules, or at least of comparatively small polymerized groups, but the molecules orient themselves, as the solution cools, so as to leave a minimum of free energy, the most active acid groups tending to unite with the most active basic groups until a continuous network is formed throughout the system. A block of jelly might thus be looked upon as an enormous, single molecule, a view which is not radical in the light of modern theories of crystal structure.

Loeb's work on the viscosity of gelatin solutions indicates that the initial step in gelation is the combination of individual molecules to form large aggregates, possibly in a manner similar to the growth of crystals. Bogue<sup>14</sup> pictures this process as the formation of catenary threads by the union of the individual molecules end to end. The manner in which fibrous curds of soap are formed led McBain<sup>15</sup> to a similar view regarding the structure of soap jellies and solutions. He attributes the elasticity of gels to the formation of an exceedingly fine filamentous structure. Innumerable molecules placed lengthwise and held together by forces of residual valence are assumed to make up these fine threads, which may vary from a few microns to several millimeters in length.

Considering the nature and variety of the amino acids composing the gelatin molecule, we should not expect the polymerization of gelatin to take place along a single line, but in every direction and probably with cross chains growing to sup-

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<sup>13</sup> "The Structure of Organic Jellies," H. R. Procter, *Proc. Seventh International Congress of Applied Chemistry*, London, 1909

<sup>14</sup> "The Chemistry and Technology of Gelatin and Glue," R. H. Bogue, McGraw-Hill Book Co., New York, 1922

<sup>15</sup> "Colloid Chemistry of Soap," J. W. McBain, *Brit. Assoc. Advancement Sci., Third Report of Colloid Chemistry*, 1920, 2

port chains increasing in length in other directions. The increasing viscosity of gelatin solutions with time, upon cooling, would thus be attributed to the increasing size of the particles; the formation of a rigid jelly to the final union of the large particles, forming a structure continuous throughout the entire system.

Graham showed long ago that the velocity with which crystalloids diffuse through gelatin jellies is only very little less than the velocity through pure water. This slight reduction in velocity is in no way comparable with the apparently great physical difference in state between the jelly and water. Although the viscosity of the jelly is too great to be measured, simple molecules move through it as though in a medium of viscosity nearly that of water. The network theory explains this by assuming that the diffusing substance actually is moving through the pure water, or aqueous solution, in the interstices of the network.

Thompson<sup>16</sup> has shown, from the work of Dumanski,<sup>17</sup> that the conductivity of a solution of KCl in gelatin jelly is no less than in pure water when a correction is made for the small volume actually occupied by the gelatin network, whereas, if the apparent viscosity had any effect, the conductivity should be reduced by the gelatin to a minute fraction of its value in pure water.

The vapor pressure of even a 20 per cent. gelatin jelly is practically the same as that of water, indicating the presence of pure water in accordance with the network theory.

By placing a strain upon gelatin jelly in one direction, double refraction is produced, a property always associated with a definite structure and with anisotropy. Even dilute solutions of gelatin show double refraction on compression or when passed between two cylinders rotating in opposite directions. With increasing strain, the effect is increased up to a point corresponding to an elastic limit.

The fact that the viscosity of gelatin solutions is lowered by simply agitating the solution is another piece of evidence in favor of the existence of structure, even in gelatin solutions, and

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<sup>16</sup> "Structure of Gelatin Solutions," F. C. Thompson, *J. Soc. Leather Trades Chem.*, **3**, 209 (1919)

<sup>17</sup> *Z. physik. Chem.*, **50**, 553 (1907)



still further evidence is furnished by Loeb's work on the viscosity of gelatin solutions and by Bogue's measurements of plasticity.

That gelatin jellies are truly elastic and follow Hooke's law may be taken as proved chemically by the agreement between calculated and observed results in Table I. Sheppard and Sweet<sup>18</sup> proved by measurements of rigidity that gelatin jellies follow Hooke's law nearly up to the breaking point.

#### RESTATEMENT OF THE THEORY

According to the theory, when a block of gelatin jelly is immersed in a solution of hydrochloric acid, the solution passes into the jelly, filling up the interstices of the molecular network. Of the ionized gelatin chloride, which then forms, the chloride ions remain in the solution in the interstices while their corresponding gelatin cations form part of the network and are not in solution in the same sense as the chloride ions. Because these chloride ions are balanced only by the positive electrical charges on the gelatin network, there results an unequal distribution of all ions between the external solution and that absorbed by the gelatin such that the total concentration of ions is always greater in the jelly than in the external solution. In tending to diffuse into the external solution, the anions of the protein salt exert a pull upon the cations forming part of the gelatin network, causing an increase in volume of the jelly directly proportional to the excess of concentration of diffusible ions of the jelly over that of the external solution.

The degree of swelling of any protein in contact with any electrolyte is increased by increasing the proportion of the protein existing in the ionic, or electrically charged, form and decreased by increasing the concentration of any ions which do not increase the proportion of ionized protein.

It is believed that this theory is proved and has a fundamental bearing upon the whole field of colloid chemistry.

<sup>18</sup> "The Elastic Properties of Gelatin Jellies," S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.*, **43**, 539 (1921)

## THE THERMOCHEMISTRY OF PROTEIN BEHAVIOR

BY J. HOWARD MATHEWS AND BEN W. ROWLAND

The complex chemistry of proteins has been the subject of an enormous amount of research, much of which has been carried out by highly competent investigators, but, as is well known, the theories of the chemical and physical behavior of the proteins are still a matter of debate, especially since recent advances in Colloid Chemistry have added the complications of surface phenomena to the complexity of protein chemistry in a strict sense of the word.

Proteins are generally thought to be capable of existing in a colloidal state, and if this be true, many of the physical and perhaps some of the chemical properties of these substances may be understood when more data on the colloidal behavior of proteins are obtained. Numerous experiments have been made on the viscosity, osmotic pressure, rates of swelling and related physical properties of proteins, and have marked a notable advance in the subject, despite the fact that several different theories seem to be generally borne out by the results of such investigations.

It is not easy to discover the point at which protein behavior ceases to be a strictly chemical phenomenon, *i. e.*, one of typical chemical combination, decomposition or hydrolysis, and becomes a colloidal phenomenon. Perhaps there is not a sharp line which one may draw, on one side of which the proteins exist as true molecular solutions, capable of entering into chemical reactions, and on the other side of which the proteins exist as colloidal suspensions, exhibiting properties characteristic of such systems, being subject to marked modifications in physical properties, because of adsorption, degree of dispersity and other typical colloidal considerations. In fact, there are those who feel that the chemistry of gelatine, in a true molecular solution, if it may exist as such, persists with little or no modifications when such solutions pass gradually or suddenly into colloidal systems. It is not likely that the measurements of physical properties alone will afford conclusive evidence for or against such arguments, since these physical properties are

more or less indirect evidence of the fundamental nature of the proteins, being sufficiently removed from these fundamental properties to permit the existence of the several different theories referred to above.

The present preliminary paper does not presume to settle all or any of these highly involved arguments; but it offers a new method of attacking the problem, *i. e.*, from the standpoint of thermochemistry, or of energy changes in protein solutions when mixed with electrolytes. Such energy changes, if measurable and susceptible to correct interpretation, would seem to afford an important means of investigating the more fundamental nature of colloidal proteins.

Gelatine, being a typical protein substance, and one which is obtainable in a reasonably pure form, has been used in this

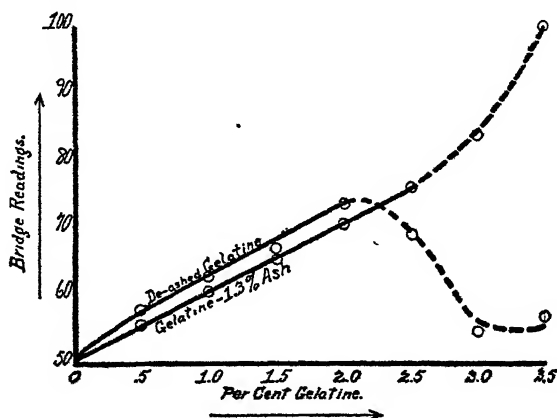


Fig. 1.

investigation. The adiabatic calorimeter, adapted for measuring excessively small thermal changes and fitted with a special device for mixing two solutions quickly, has been described in this symposium by Dr. F. L. Browne.

A series of experiments was conducted by adding a fixed quantity of  $N/2$  HCl to gelatine solutions of varying per cent. composition, all of the measurements throughout the investigation being carried out at  $40^{\circ}\text{C}$ . to prevent gel formation. A series of runs was made first on a sample of gelatine containing 1.3% ash. The curve was repeated on special de-ashed, iso-electric gelatine which was prepared by electro dialysis in the East-

man Research Laboratories, and which contained 0.05% ash.

This diagram shows bridge readings, corresponding to temperature changes, plotted against per cent. composition of gelatine solutions to which 10 cc.  $N/2$  HCl is added. It will be observed that these two curves show interesting similarities and a very striking dissimilarity. For low concentrations of gelatine solutions, the heat effect is a straight line function of the concentration, the de-ashed curve being slightly above that for the gelatine containing the ash. It is possible that the presence of ash diminishes the additional quantity of electrolyte which the gelatine may adsorb, if the ash is itself adsorbed. This would explain why the de-ashed curve lies slightly above the other. At a certain range of concentration, *i. e.*, at about 2% of gelatine, the thermal changes rise indefinitely, in the case of the gelatine containing the ash, and fall indefinitely in the case of the de-ashed material. The calorimetric experiments could not be checked accurately beyond this point. It should be borne in mind that the significant portions of these curves lie entirely within a temperature range of  $0.003^{\circ}\text{C}.$ , which corresponds in this calorimeter to about 0.7 of a small calorie, a fact which seems to indicate that we are dealing here with heats of adsorption, which will be mentioned later. The fact that the measurements become indefinite at a certain point may be due to the possibility that beyond that point we have sufficient gelatine, so that there is no longer enough acid to provide for maximum adsorption and that the heat effect is somewhat dependent upon the rate of mixing and stirring. We have as yet no explanation for the rise of one curve and the fall of the other.

An experiment was conducted in a manner similar to the foregoing, except that a concentration of NaOH was used, containing that quantity in 10 cc. of a  $N/2$  solution, *i. e.*, equal to the 10 cc.  $N/2$  HCl added. This gave a heat effect so great as to render accurate observation impossible, since the adiabaticity was lost, but amounted to about one hundred times that observed in the case of gelatine of equivalent concentration (taking the chemical equivalent of gelatine as 900). It was thought that this great difference might be largely due to the possibility that if a chemical compound were formed between the acid and gelatine, the resulting substance might be, and

probably would be, very highly hydrolyzed. The following experiments were made to determine, if possible, whether chemical reaction had taken place between the gelatine and acid.

Heats of mixing of the 10 cc.  $N/2$  HCl with several concentrations of glycine were determined. The quantities of glycine were 0.13, 0.26 and 0.39 grams respectively, the latter being the equivalent of the 2% gelatine solution, and approximately equal to the 10 cc.  $N/2$  HCl. (The same volume of water was used as for gelatine, *i. e.*, 200 cc.). These heat effects were likewise small, but decidedly larger than those obtained from the gelatine, but here again, it seemed that the difference might be largely due to the differences of hydrolysis of gelatine hydrochloride as compared to glycine hydrochloride.

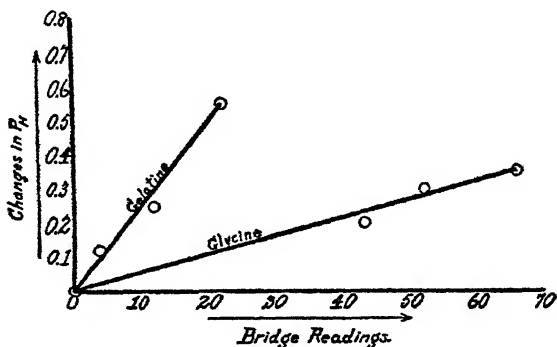


Fig. 2.

It appeared that hydrogen electrode measurements might offer some explanation of these thermal data.  $p_H$  readings were taken on several gelatine solutions of different concentration after the addition of the acid, and also on the glycine solutions after addition of the acid, in order to compare both to the  $p_H$  obtained from a solution of 10 cc.  $N/2$  HCl in the same volume of pure water. (The gelatine used in this connection was the de-ashed material). These observations gave the changes in  $p_H$  of the HCl solutions, brought about by the addition of gelatine and glycine respectively.

When these values are plotted against the thermal changes accompanying them, the curves shown on the preceding diagram are obtained.

It will be observed that in the case of glycine, which probably undergoes a chemical reaction with HCl, that for a given change in  $p_H$ , we find a decidedly greater heat effect than in the case of gelatine. The farthest points on these two curves indicate equivalent quantities of these two substances which are in turn equivalent to the 10 cc.  $N/2$  HCl added. These curves indicate that hydrogen ions are being removed from solution by a different process in the two cases, the difference giving rise to the different energy changes. For a given consumption of H ions by a chemical process we might expect a greater energy change than that taking place when the same quantity of H ions is removed by adsorption. If this be true, the glycine curve would be expected to show greater heat effect than that for gelatine, *i. e.*, if we have chemical reaction in the former and adsorption in the latter. Perhaps there is a slight chemical combination in the case of gelatine which gives rise to almost all of the heat effect, adsorption taking place at the same time with very low energy change, but this does not seem likely.

These experiments are being extended in this laboratory with a view of obtaining such thermodynamical data as will afford more definite conclusions than are possible at present.

Acknowledgment is given to Dr. Browne for his original conception of the possibilities in this method of investigation.

#### JOINT DISCUSSION ON JACQUES LOEB'S PAPER HOFMEISTER ION SERIES

J. A. WILSON'S PAPER

#### THE SWELLING OF PROTEIN JELLIES

AND J. H. MATHEWS AND BEN ROWLAND'S PAPER ON  
THE THERMOCHEMISTRY OF PROTEIN BEHAVIOR

E. F. BURTON: I have been told that you can add a considerable amount of acid to a gelatin solution without making a noticeable change in hydrogen ion concentration. Is that true?

J. A. WILSON: No. It is true, however, that the change is very much less than is observed when the same amount of acid is added to pure water.

T. SVEDBERG: The theory that Dr. Wilson has outlined

is certainly a very remarkable advance and I think we all have a feeling that this is the first time that an honest attempt has been made to account quantitatively for the swelling of a jelly caused by an electrolyte. That is of extreme importance, and I think we have to analyze in every detail the fundamental assumptions on which the calculations are based. It is obvious from investigations of the structure of jellies that discontinuities exist of quite another order of magnitude than those of the solutions described by Donnan. It may not be permissible to speak of concentrations within the jelly in the same sense as in Donnan's solution, for this reason. If the discontinuities were sufficiently great, there would be a fall in total concentration of ions in passing from the surface of the gelatin structure to some point within the jelly, but further removed from the actual structure. I do not know, but I think that might cause some trouble.

J. A. WILSON: The point raised by Professor Svedberg is theoretically correct. If the interstices of the gelatin network are relatively very large, the absorbed solution will be separated into two phases: one of higher total concentration, in the immediate vicinity of the gelatin network, and one of lower concentration, in the portions of absorbed solution further removed from the network, as Professor Svedberg suggests. On the other hand, if the interstices are relatively small in magnitude, the chloride ions of the gelatin chloride will be free to move everywhere throughout the absorbed solution, in which case the solution would consist only of a single phase of uniform concentration. It is easy to show, where the absorbed solution is divided into two phases, that the discontinuous phase must have the same concentration as the external solution surrounding the entire block of jelly. In the theory just outlined, it is assumed that the absorbed solution is continuous and consists of a single phase and the practically perfect agreement between calculated and observed results would seem to prove the correctness of the assumption for this particular series of experiments. We have discussed this phase of the problem in an earlier paper [*J. Am. Chem. Soc.*, 40, 892 (1918)].

T. SVEDBERG: Studies of the structure of jellies show that the magnitude of the discontinuities in the structure of a jelly is of the same order as the magnitude of the volume of a solu-

tion within which, according to Smoluchowski, the fluctuations in concentration are appreciable and must be considered. In such an ultramicroscopic structure of a jelly, electro-neutrality cannot be assumed to exist as was safely done in the macroscopic cells used in the derivation of the original Donnan equilibrium. The keynote of my argument is that the distribution may not be sufficiently uniform to justify the application of these equations. Due to the stability of the jelly structure, there may be permanent differences in concentration in various points of the jelly.

N. E. GORDON: I do not see how the Donnan equilibrium applies to gelatin jellies, since you have no membrane.

J. A. WILSON: The theory I have presented is different from Donnan's theory in that there is no membrane, the equilibrium conditions being determined by the cohesive forces of the gelatin. The similarity between the two theories lies in the fact that each describe a system divided into two phases and that the distribution of ions between these two phases is governed by Donnan's equation of equality of products.

F. E. BARTELL: In the experiment described, had the gelatin been swollen in water before being placed in the HCl solution?

J. A. WILSON: The experiments were repeated many times and were done at one time or another in both of the ways you mention. In some experiments, we washed the gelatin plates in very dilute HCl to remove impurities before starting the experiments and the results were very little different from those with untreated gelatin.

F. E. BARTELL: Does your theory explain why gelatin, gluten, and many other materials show the same type of curve on both the acid and alkaline side?

J. A. WILSON: Yes. The similarity of curves for different materials is accounted for by the family of curves shown in Fig. 3.

F. E. BARTELL: Have you then an explanation as to why it is that the swelling effects parallel the osmotic effects?

J. A. WILSON: Because the swelling is directly due to the osmotic forces.

F. E. BARTELL: Am I correct in understanding that the swelling effect is assumed to be due to a pulling outward of the gelatin molecule?



J. A. WILSON: The total concentration of ions is greater inside the jelly than outside. Hence there will be a force exerted in the direction tending to equalize differences in concentration and the volume of the jelly must increase accordingly until the outward pull is balanced by the cohesive forces of the jelly structure.

F. E. BARTELL: It might be interesting to point out a striking relationship between swelling effects and osmotic effects. Take for example, the curves you have already seen on the board. Consider first the case of osmotic effects. Curves of the following types will result (indicating osmose *vs.* concentration). Now if you will take almost any colloid material and test the swelling effect of it and of gelatine, you will find marked similarity and will find that the swelling effect is just opposite the osmotic effects with these materials when used as a membrane. In those cases in which one obtains an abnormally positive osmose, one will obtain a shrinking effect of the colloid. In case the osmose is negative one will obtain a swelling effect of the colloid. I prefer to think of membranes within gels of such a structure such as Prof. Svedberg indicated. Suppose we picture a single capillary pore. The actual facts are that when the material in question is charged negatively to the solution and when the orientation of the system is as indicated, negative within, we will have a passage of liquid inward and a consequent swelling effect. That would represent the condition with an alkaline solution. Take the same gel in an acid solution, if it is first electro-negative to the solution; the hydrogen ion is the more rapidly moving ion and we find that it so happens that in every case, when the electrical orientation of the system is set up in this manner we obtain migration of liquid outward and a simultaneous shrinking effect. Suppose we immerse gelatine in acid and obtain this type of electrical orientation (indicating), we would then obtain a swelling effect. It seems that the general principle just given will explain the swelling and shrinking of gel fully as well as to assume that a molecule or ion in pulling outward tends to enlarge the entire surface. In order to include all the types of electrically oriented systems we might consider the fourth type, which is that represented by almost any colloid material in a solution of alum. In this case the membrane material becomes positive through adsorption of cation,

to the liquid negative and here the anion diffuses inward more rapidly than the cation with the result that the electrical orientation is such that the liquid layer is pulled outward, causing a shrinking of the colloid. So we do find apparently, without any exception, that the swelling and shrinking effects fit in absolutely with the anomalous osmose effects.

J. A. WILSON: Why resort to speculation of this kind when we have been able to calculate the swelling of gelatin quantitatively over a wide range and Loeb has demonstrated repeatedly that other properties of gelatin systems, such as osmotic pressure, viscosity, and electrical properties, can be explained on the same basis?

F. E. BARTELL: The theory as presented by you was at the outset based on an assumption.

J. A. WILSON: The assumption to which you refer is simply that the amount of hydrogen ion combined with the gelatin is determined by the product of the concentration of neutral gelatin and free hydrogen ion. I am not so sure that this assumption is not widely accepted, even though some may prefer to regard the combination as something other than strictly chemical.

F. E. BARTELL: In answer to the question as to the speculation connected with the other theory, is it not generally accepted that we have a double layer, that we have a potential set up due to difference in migration velocity?

H. S. TAYLOR: As a person standing at the sidelines looking at the show, I might ask, can the theory which has been presented on the board last be subjected to the same quantitative treatment that Dr. Wilson's presentation has been, because the language that Dr. Wilson talks is the language which everybody believing in the first and second laws of thermodynamics can understand? Now, can the same thing be said about the quantitative mathematical treatment of Dr. Bartell's theory? As far as the argument goes at the present time the sole quantitative treatment of this subject has come from the one side and I would like to hear some of the arguments on the other side regarding that matter.

F. E. BARTELL: I would like to call attention to the fact that practically all the quantitative evidence appears to come from a single source, Dr. Loeb. I for one have not been able to duplicate many of the quantitative results.

H. S. TAYLOR: I might then call your attention to a similar historical case of difference of opinion. There was a man in London and two in the University of Berlin who were working on the same thing and could not get the same results no matter how hard they tried. They therefore finally decided that it was not a very long distance from Berlin to London, and they traveled to London and said, "Let us do these experiments together," and they did so and they came to a very satisfactory conclusion. I do not see why it is necessary in the case of a person living in New York and one in Chicago, for the man living in New York to say "my results are right and his results are wrong," and *vice versa*. If we can come for a week to Wisconsin to talk about colloid chemistry we can get together on any matter and make experiments to which both of us subscribe. It is useless for us to talk and say that we can't get the same experimental results. Let us get together in the same laboratory, over the same instruments, at the same time, and do the same tests together and then see what our results will be.

J. H. MATHEWS: I might say in that connection, that the University of Wisconsin offers you its laboratory and equipment if you care to use them.

J. ALEXANDER: We have here a large number of minds and a large number of experimental facts, and a large number of very excellent mathematical equations, but we must never overlook the fact that mathematics is exactly like a purse; you can't get anything out of it that you don't put into it. Everything depends upon your fundamental assumptions, and here in this case we have pretty positive experimental evidence that one assumption is erroneous. All the facts are not mentioned, evidently, in all cases by those who are arriving at these theories. It is very interesting on the other hand to know what Donnan said in New Haven. You will recall that he pointed out very well that his equilibrium does not depend at all upon the assumption that there is any chemical combination.

I do not know as I want to take any more of your time, because I think you will find in the monograph No. 11 of the American Chemical Society some further details regarding objections to some of the theories that are brought up. In dealing with the gas laws, if you work within certain limitations

the figures that are afterwards introduced do not enter as a factor;  $a$  and  $b$  don't worry us. And so if we wish to choose certain limitations by experiments we can prove pretty nearly anything within the limit of experimental error. Well, I will go no further, I only wish that I had the opportunities that some of the men have who have university facilities. Perhaps it would be possible to make experiments which would demonstrate these matters. In conclusion, there are usually a great many ways to explain how Cock Robin came to his death, and we must not assume that the experiments or the facts themselves are not correct because we do not follow the particular theory.

J. A. WILSON: Mr. Alexander's remarks have no bearing at all upon the correctness of the theory presented. The theory makes the assumption that the removal of hydrogen ion from solution is governed by the equation:  $(G) \times (H^+) = K(GH^+)$ . What Donnan said in effect at New Haven was that it makes no difference to the theory whether you call  $GH^+$  a chemical compound or prefer to regard it as  $H^+$  adsorbed by  $G$ , whatever adsorption may mean in this sense, and it is clear that this is true. The possibility that gelatin may be a mixture of different proteins has nothing to do with the theory, although the values of the constants in the equations must, necessarily, depend upon the proportion of the different proteins making up the sample under observations. The quantitative chemistry of nitrogen is none the less sound because what we call nitrogen is really a mixture of isotopes.

Regarding the Hofmeister series, it is admitted that equimolar solutions of different acids and salts affect the swelling, osmotic pressure, and viscosity of gelatin systems differently, but this is due to their effects upon the hydrogen ion concentration of the solutions and not to any supposedly different effects exerted directly upon the properties of the gelatin, as Loeb proved by making comparisons at definite  $p_H$  values.

R. A. GORTNER: I would like to make just a few remarks in regard to the last three papers. First, in regard to that assumption of Dr. Wilson's. I do not believe that it is correct, and I have certain evidence that bears out the conclusion, and the picture that Dr. Bartell put on the board came with rather a shock to me because it was just what I have been

looking for. With flours we found that the imbibition capacity of the proteins of the wheat is determined by the colloidal nature of the gluten proteins. We find that the gliadins in a very strong flour, and in a weak flour obey essentially the same colloid laws; the glutenin proteins, however, differ widely in their colloidal behavior. The hydrogen ion concentration is an extremely important factor, but the glutenins at equivalent concentration of protein, containing the same amount of ash, binding the same amount of acid, at the same hydrogen ion concentration, may differ 300 per cent. in viscosity. That picture is to my mind the essential thing, that the same protein from two biological sources, will differ in its hydration, in its osmotic effects, and I do not see how you are going to explain that on the basis of the assumption given.

Now, this last paper is extremely interesting to me, and I would like to tell Dr. Mathews that I have some proteins that he would find exceedingly interesting. There is a paper by Miss Lloyd in which she worked with gelatin, measuring its acid binding capacity, and she has come to the conclusion that the acid was bound chemically on the basic amino acids. In the first place she made the assumption that the hydrogen ion concentration of hydrochloric acid can be calculated from the dissociation constant, and it can't. If you take her data and recalculate it on the basis of actual (instead of calculated) hydrogen ion concentration, her broken curve becomes a perfectly smooth curve. The difference that the various workers come to, depend very largely upon the fact that they work on different proteins. That is, the colloidal behavior of a protein may be dependent upon the conditions under which it was laid down in the tissues, and upon the method by which it was isolated and purified. Hysteresis (used in the colloidal sense) is very marked. So we have started at Minnesota, or Mr. Hoffman has, a study of the proteins from all the cereal grains, and we can get protamines containing from six to twenty per cent. of basic amino acids and have tested the hypothesis that the basic  $\text{NH}_2$  groups are responsible for acid binding capacity. But we did not get a difference of binding capacity between six per cent. and twenty per cent. proteins. Gram for gram the twenty per cent. basic amino acid proteins of the same type bind just as much acid or alkali as those which have

almost no basic amino nitrogen and I do not see how you are going to explain that on chemical combination grounds.

E. F. BURTON: What was your test for acid binding?

R. A. GORTNER: We used both the hydrogen electrode and the electrolytic conductivity method in all cases.

DR. HIRSCHFELDER: I would like, in connection with the first paper, to mention the fact that in 1916<sup>1</sup> I found that if one raised the acidity of a solution which contained powdered fibrin in suspension to a constant hydrogen ion concentration (using as an indicator dimethylaminoazobenzol, which turns at a point between  $p_H-3$  and  $p_H-4$ ) the swelling of the fibrin in hydrochloric, acetic, tartaric and phosphoric acids, at this concentration of hydrogen ions, was practically uniform, and that this uniformity of swelling was approximately the same whether the acidity had been produced by varying the concentration of either the hydrochloric or the other acids. On the other hand, the swelling of the fibrin was very markedly decreased in the presence of sulphuric acid. The hydrogen ion concentration in these experiments corresponds to the point at which Dr. Loeb some years later found the point of maximum swelling on the curve for gelatin. My paper was published in the Journal of the American Medical Association in 1916, and represents, I believe, the first in which the deviation from the Hofmeister theory was determined.

E. B. SPEAR: I should like to call attention to the fact that we are dealing here with very complex and difficult systems, so why not, for the sake of studying swellings, go to something that is very much more simple. We can choose rubber in benzol, for instance. If we could get somebody to work on some systems of that sort, and I know of no better one than rubber, the fine work that these gentlemen are doing would get us somewhere. I believe we could get along faster than by working with these extremely complicated systems to begin with. Let us eliminate some of these complicated factors and get the fundamental theory of the swelling settled in that way.

S. E. SHEPPARD: I think Dr. Spear's suggestion is a very good one, especially the point of having some of these factors

<sup>1</sup> A. D. Hirschfelder, "Studies on the Effects of Acids," *J. Am. Med. Assoc.* 67, 1891 (1916)

eliminated, and in that connection I would like to ask Dr. Wilson what he considers to be the character of the swelling at the iso-electric point, and how far he considers the differences of the same protein can be carried in his explanation. The constant in the application of Hooke's law seems to come into play. The differences in the swelling of one and the same protein—I will take gelatin for instance—there are not only differences in the absolute swelling but in addition to that there are also differences in the directions of the swelling. It is assumed in Procter and Wilson's theory that the swelling is uniform in all directions. That does not affect the equations fundamentally but actually it is almost impossible to get jelly to swell uniformly in all directions. I am bringing this point out rather to get some ideas as to what causes that, rather than to bring it up in the light of any objection to the fundamental theory of Procter and Wilson. It is rather with the object of seeing if the aggregates, the structural conditions, and so forth, which were emphasized by Dr. Svedberg, can be brought in to explain the difference of swelling in different dimensions that I bring this up. The swelling at the iso-electric point, which is quite considerable, should be independent of the electric equilibrium in the system, so that in the case where we have protein swelling determined upon these conditions it would to a greater degree satisfy most of us.

J. A. WILSON: The swelling of the gelatin at the iso-electric point may be attributed to two different causes. The equations given apply to both acid and alkaline swelling. Given the constants, in the two cases, it is possible to calculate the degree of swelling at the iso-electric point, which is measured by the sum of the positive and negative charges on the gelatin, which are equivalent in value. But, as Dr. Loeb has pointed out, we must also include the effect of the hydration of the gelatin at the iso-electric point, where swelling due to hydration would consist of a greater portion of the total swelling than at any other point. Dr. Sheppard has demonstrated the importance of the previous history of the gelatin in swelling and this is intelligible in view of the fact that the amount of swelling is determined by the bulk modulus of elasticity of the gelatin. The structure of a gelatin dispersion at the moment of setting must, in a large measure, determine the direction of

the swelling forces, as well as their magnitude, when the dried gelation is placed in water at the iso-electric point.

R. A. GORTNER: In regard to that last remark of Dr. Wilson, I would like to call attention to a paper [*Proc. Soc. Exper. Biol. Med.*, 19, 257-64 (1921)] in which I prepared gelatin granules which were of approximately uniform size, and they had been prepared under different conditions so as to produce different histories. They swelled differently in water; they also swelled differently in solutions of acids, and differently in the different solutions of acids at the same hydrogen ion concentration, so that your histories do carry over.

J. A. WILSON: In that case the different histories apparently were responsible for different values for the bulk modulus. Procter's paper of 1911 was along similar lines. The previous history of the gelatin determines the value of  $C$  in our equations. Regarding certain anomalous effects in osmotic pressure, mentioned by Dr. Gortner, account must be taken of the fact that gelatin dispersions are not entirely truly molecular ones. When a dispersion containing gelatin particles as well as molecules is separated from a protein-free aqueous solution by a semi-permeable membrane, the system divides itself into three distinct phases. As an example, we might mention the case of an acid solution; here the hydrogen ion concentration would be greatest in the outside aqueous solution, of intermediate value in the gelatin solution surrounding the gelatin aggregates, and lowest in the solution absorbed by the aggregates. All three phases must be recognized in any quantitative calculation.

R. A. GORTNER: Isn't that exactly what we are dealing with? We are dealing with gelatin aggregates. I would like to know what a gelatin aggregate is if it is not a colloidal particle, and if it is, then we have colloidal reactions.

J. A. WILSON: There is still a great deal of confusion over what is meant by colloidal reactions. Dr. Loeb has introduced a new conception of colloidal behavior that merits the most careful study. He has shown that a system exhibits colloidal behavior when only one kind of ion is prevented from diffusing freely from one phase to another.

H. S. TAYLOR: I would like to ask Dr. Wilson something with regard to point of view. I think considerable injustice



is caused to those who are opposed to the chemical theory by drawing in the Donnan membrane equilibrium. Would it not be possible to treat the whole subject as a distribution of hydrochloric acid and the treatment then would be a mere application of the distribution law, which is a great deal older, and which, like Prof. Donnan's theory, is entirely in agreement with the second law? It seems to me that one can regard this whole subject as a question of the distribution of hydrochloric acid, one part in the gelatin phase and the other in the water phase.

J. A. WILSON: What Dr. Taylor says is quite true. Donnan's name is brought in as a tribute to his genius in recognizing the application of these fundamental principles to membrane equilibria. It was through Donnan's work that Procter first recognized their application to the swelling of gelatin and Loeb, later, their application to other manifestations of colloidal behavior.

A. L. FERGUSON: I am not at all qualified to speak as a colloid chemist, but I have been doing some experiments which are related to this subject, and that may or may not qualify me to speak. Some years ago, some of you will recall, an article was published concerning the influence of gelatin on silver nitrate, and that was later followed by a similar piece of work by the same man on the influence of gelatin on zinc sulphate, and so forth. The results he obtained struck me as being rather remarkable. He found, for instance, that by adding small quantities of gelatin he could decrease the transference number of the silver ion, and also in the case of the zinc and copper ions. This decrease was in proportion to the quantity of gelatin added. This decrease went on so far, however, that by adding a sufficient amount he even got the nitrate ion and the gelatin and nitrate gelatin complex moving toward the positive electrode, and he got more current than he should. That didn't sound at all reasonable, so I thought it might be worth while to try to duplicate that work. Instead of using salt solutions we had a set-up for working with transference numbers of acid solutions. So, using that set-up we measured the transference of sulphuric acid by the concentration method and then put in varying quantities of gelatin. We found that the transference number of sulphuric acid is

about 88, and by adding a little gelatin it became less, and finally we put in a ten per cent. solution and the transference number dropped to about 30. On these same solutions we carried out hydrogen ion measurements, and we found out—this was pretty quantitative—that the amount of decrease in activity was directly proportionate to the amount of gelatin material. This was also true in hydrogen ion concentration. It looked to us at the time that the most logical way of explaining this was that the sulphuric acid combines with the gelatin and assumes a positive charge, and that with a sulphate you get a negative, and that explained very well all the data which we have obtained. I then thought it well to extend that work to the salt and at the present time we are carrying out work along that line, trying to duplicate that work. I might say that so far as these rough results have been carried out up to the present time we find no effect of gelatin on silver nitrate. That was as we expected; that with neutral salts that would be the case.

To carry this work a little further in another field, we took the decomposition of sulphuric acid alone and then in the presence of varying quantities of gelatin added neutral salts and also sodium hydroxide. The results are not all complete yet but the indications are at the present time that this work confirms the work done on transference numbers, in other words, the results can all be explained on the basis of the combination between gelatin and sulphuric acid in the ordinary chemical way.

J. ALEXANDER: I would just like to add a word of appreciation to Prof. Mathews and his co-workers. They seem to be getting at some very valuable information. At the present time when everybody is making experimentations with which to prove that somebody is right or disprove something else, it is very interesting to find that there are men who are trying to find out what the truth really is. It seems to me that all scientific men should strive for the truth primarily, and the experimental means should be *any* experimental means. We should be prejudiced against none.

## ON THE THEORY OF THE LYOPHILIC COLLOIDS AND THE BEHAVIOR OF PROTOPLASM

BY MARTIN H. FISCHER

### ON THE THEORY OF THE LYOPHILIC COLLOIDS

In connection with a colloid-chemical study of the soaps an attempt was made some years ago to outline a *general theory of the lyophilic colloid state*<sup>1</sup> which, it seemed to us, explained satisfactorily not only the behavior of soap systems but that of lyophilic colloids in general. This theory went back to a suggestion originally made by W. B. Hardy,<sup>2</sup> though afterwards discarded by him, that colloid systems are essentially mixtures of two mutually soluble substances, to the physico-chemical peculiarities of such systems noted by J. Friedländer<sup>3</sup> and V. Rothmund,<sup>4</sup> the declaration by D. Konowalow<sup>5</sup> that such systems, at their critical temperatures, are colloid and the clear cut definition of these systems as emulsoids by Wolfgang Ostwald.<sup>6</sup>

The situation for the lyophilic colloids, as we see it, is represented by the diagrams A and B of Fig. 1. Diagram A is representative of systems in which the two phases are liquid at the temperatures employed, diagram B when the separating phase is solid or crystalline. If, for illustration, the system soap-water is chosen (say, potassium oleate-water in illustration of diagram A and sodium stearate-water in illustration of diagram B) the entire set of systems illustrated in the two diagrams may be obtained with mere variation in temperature. At higher temperatures, the soap dissolves in the water and there results a "true" solution. This matter is represented by the region marked A in the diagrams (the soap is dispersed molecularly or ionically in the solvent). As the temperature is lowered, the solubility of the soap in the water is decreased and

<sup>1</sup> Martin H. Fischer, *Science*, **48**, 143 (1918); *ibid.*, **49**, 615 (1919); *Chem. Eng* **27**, 186 (1919); "Soaps and Proteins," New York, 1921, 64

<sup>2</sup> W. B. Hardy, *J. Physiol.*, **24**, 158 (1899); *Z. physik. Chem.*, **33**, 326 (1900)

<sup>3</sup> J. Friedländer, *Z. physik. Chem.*, **38**, 430 (1901)

<sup>4</sup> V. Rothmund, *Z. physik. Chem.*, **63**, 54 (1908)

<sup>5</sup> D. Konowalow, *Drudes Ann.*, **10**, 378 (1905)

<sup>6</sup> Wolfgang Ostwald, *Kolloid-Z.*, **1**, 335 (1907); "Introduction to Theoretical and Applied Colloid Chemistry," 2nd ed., New York, 1922, 95

as the saturation point for the lower temperature is lowered, the solubility of the soap in the water is decreased and as the saturation point for the lower temperature is attained, the soap particles assume more than molecular size. By definition, therefore, we approach with falling temperature the realm

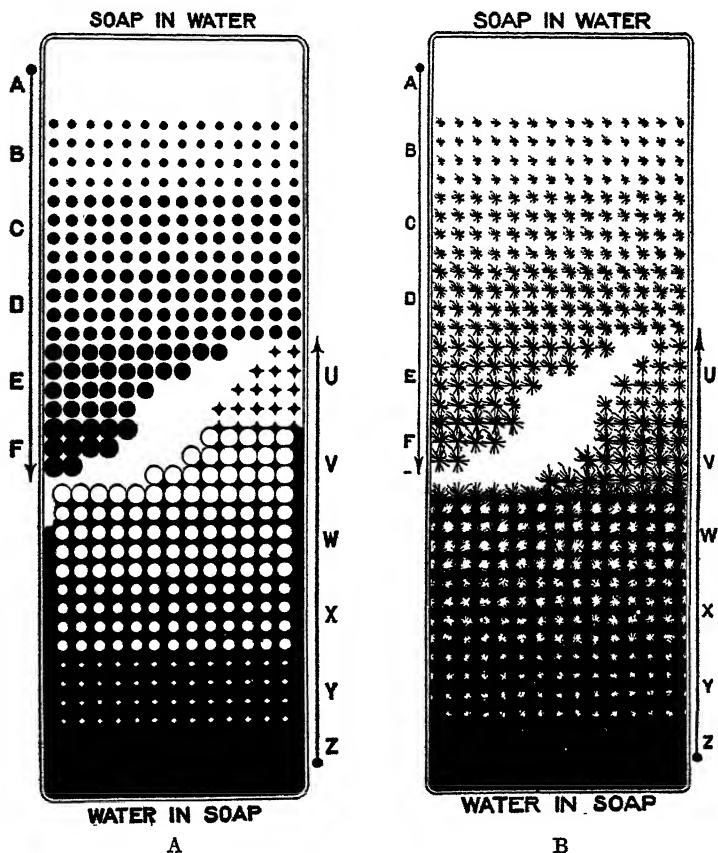


Fig. 1.

of the colloids, or that of dispersions of one material in a second with the degree of dispersion showing dimensions greater than the molecular. This gradual increase in the size of the soap particles (or increase in their number) with lowering of the temperature is represented by the regions B, C, D, E and F.

Such supersaturation with agglomeration of particles while yielding us a colloid system does not yet tell us whether such will be lyophobic or lyophilic (or, depending upon the solid or liquid nature of the separating phase, a suspension or an emulsion colloid). *The lyophobic colloid results when the solvent is not soluble, the lyophilic when the solvent is soluble in the precipitating phase.* When soap falls out of solution from such a solvent as allyl alcohol the former of these possibilities is satisfied (and we get a lyophobic colloid); when it falls out from most other alcohols or, as in our illustration, from water, the latter is satisfied (and we get a lyophilic "sol" or "gel"). The black circles or crystal clusters in the diagrams of Fig. 1 represent more, therefore, in the latter instance than precipitates of pure soap; they are this, plus a certain amount of the water (or other "solvent") dissolved in them.

At a sufficiently low temperature the soap aggregates will have become so large or so numerous as to touch and coalesce. This process continued sufficiently must yield ultimately a single system in which the soap has now become the "solvent" for the water. Diagrammatically this situation is represented by the zone Z of Fig. 1.

Between the upper extreme (A) of a solution of the soap in the solvent and the lower extreme (Z) of a solution of the solvent in the soap, there exist two main zones of mixed systems,—one below the upper (B, C, D and E) consisting of a dispersion of solvated-soap in the soaped-solvent, and a second above the lower (Y, X, W and V) consisting of soaped-solvent in the solvated-soap. These two mixed systems (if the soap is liquid) are in essence emulsions, but of opposite type and as such (even when of the same quantitative chemical constitution) are possessed of totally different physical properties. The former corresponds, for example, to an emulsion of oil-in-water, the second to one of water-in-oil, and as the former (as illustrated by milk) will mix with water, wet paper and show a certain viscosity value, the latter (as illustrated by butter) will mix only with oil, will grease paper and show an entirely different viscosity.<sup>7</sup>

<sup>7</sup> See in this connection Martin H. Fischer and Marian O. Hooker, *Science*, **43**, 468 (1916); *Kolloid-Z.*, **18**, 129 (1916); *ibid.*, **18**, 242 (1916); "Fats and Fatty Degeneration," New York, 1917, 20

Returning to the lyophilic soap and the diagrams, it is obvious that as we descend, with lowering of temperature, from the region A, we pass in the regions B, C and D through increasingly viscid liquid colloid "solutions" (so-called sols) but all of them emulsions of the type solvated-soap in soap-water. In the region E, the particles of solvated soap almost touch and here the highest (liquid) viscosity is obtained. In F they do touch and now form a continuous external phase. At this point we change to the opposite type of emulsion (to one of soap-water in solvated-soap) and the previously liquid colloid becomes solid. As ordinarily put, the mixture gels.

It is of interest next to emphasize how this concept of the changes which a soap-water system suffers in passing from a liquid sol to a dry gel may help to explain some of the "strange" characteristics of colloid systems.

It is clear, first, that *this concept of the lyophilic colloid sets no limitations upon the nature of the materials that may make up such a system and makes no specifications as to the nature of the forces which guarantee its stability. They are, in general, any or all the forces which appear or are operative whenever "solution" of any kind occurs.* This is emphasized because there has been much written, for example, regarding the all-important effects of such single elements as the electrical charges, the hydrogen ion concentration, etc., in determining the stability of colloids in general or that of the lyophilic colloids in particular. We do not wish to deny that electrical charges or hydrogen or hydroxyl ions may sometimes play some rôle in determining the behavior of some colloid systems but this is an altogether too narrow view to take of the lyophilic colloids in general. Electrical forces may be apparent, for example, in systems composed of soaps and water or of proteins and water; they have to be whenever the system as a whole has any of the phase soap- or protein-dissolved-in-water present in it, in other words in all the regions of our diagrams above the level Y. But the discoverable electrical charges or the hydrogen or hydroxyl ion concentrations no more determine the properties of such colloid systems than the H or OH ions of distilled water explain its physical state; the electrical charges and the hydrogen and hydroxyl ion concentrations are only the accidental consequences of the fact that one of the phases of the colloid system

(soap or protein) is "soluble," hydrolyzable and ionizable in any excess of water that may be present. That the electrical phenomena are an accidental consequence, and not a cause of the behavior of such colloid systems is proved by the fact that soaps form as good or better colloid systems with the most varied types of "organic" solvents (as the anhydrous alcohols, toluene, benzene, chloroform or ether). And where are the electrical forces when lyophilic colloid systems are built up of nitrocellulose with ether and alcohol, agar-agar with water, or rubber with benzene? What remains are two mutually soluble substances and the forces active are any or all that appear whenever such "solution" occurs.

The diagrams serve to clarify also the colloid-chemical concepts of *hysteresis*, *gelation capacity*, *swelling* and *syneresis*.

When it is borne in mind that the absolute solubility values of any two mutually soluble substances are rarely the same and that the rates at which they go into solution into each other are usually different, it becomes apparent why, with lowering of temperature for example, a lyophilic colloid system will tend in general to set at a temperature lower than that at which it will liquefy when, on a reversal of experimental conditions, the temperature is raised. The point at which a lyophilic colloid system gels is obviously that at which the solvated colloid phase becomes the external one. The colloid system at this point still contains as an internal phase a solution of the colloid in the solvent. Gelation capacity is therefore always greater than the solvation or hydration capacity of a colloid. The latter measures the solubility of the solvent in the colloid material. The increase in the volume of the latter as the solvent is taken up is the measure of its ability to "swell." The zone Z in the diagrams covers the swelling capacity of a given material with its "solvent;" the gelation capacity embraces all the zones above this up to and including the zone V. As soon as this zone is passed, the external hydrated colloid phase may not be adequate to inclose all the solution of colloid-in-solvent, at which point the system as a whole tends to sweat, in other words, to show the characteristic phenomenon of syneresis. The failure to inclose adequately the internal phase will be more likely if one of the materials of the mutually soluble system is solid than when both are liquid, wherefore colloids

of the hydrated solid type (like sodium stearate-water, silicic acid-water) will show a greater degree of syneresis than more liquid ones (like sodium oleate-water, rubber-benzene, etc.).

#### LYOPHILIC COLLOIDS AND PROTOPLASMIC BEHAVIOR

It has been the purpose of our various colloid-chemical studies for many years past to demonstrate the analogies which exist between the behavior of various lyophilic (hydrophilic) colloids and living cells.<sup>8</sup> In these we brought proof that the laws of water absorption as observable in simple proteins under the influence of acids, alkalies and salts are identical with those which govern water absorption by living cells when exposed to the same external circumstances, obtaining in this way an understanding of the nature of water absorption by protoplasm under both physiological and pathological circumstances without recourse to the older osmotic concepts of cell structure. This colloid-chemical notion of water absorption brought us also a more satisfactory answer than did the osmotic concept to that mysterious element in the absorption and secretion of dissolved substances which expresses itself, for example, in the failure of different cells to take up in the same concentration any dissolved substance which may be borne to them from a common blood stream. The dissolved substances have a different distribution (solution) coefficient, in the different cells, the absorbing materials in them are different, or the cells show differences in chemical constitution.<sup>9</sup> The continuance of such studies<sup>10</sup> has therefore led us to define living matter as essentially a solution of water in protoplasm; the secretions from the body (like the urine and sweat) as essentially water in which protoplasmic material has been dissolved. In the diagrams of Fig. 1, normal protoplasm is therefore something which lies well below the middle of the figures while the aqueous secretions

<sup>8</sup> Martin H. Fischer, "Physiology of Alimentation," New York, 1907, 268; Martin H. Fischer and Gertrude Moore, *Am. J. Physiol.*, **20**, 330 (1907); Martin H. Fischer, *Pflüger's Arch.*, **124**, 69 (1908); *ibid.*, **125**, 99 (1908); *ibid.*, **127**, 1 (1909); *ibid.*, **127**, 46 (1909); or in connected form in "Oedema," New York, 1910; "Nephritis," New York, 1912; "Oedema and Nephritis," 3rd ed., New York, 1921

<sup>9</sup> Martin H. Fischer, "Oedema," New York, 1910, 202; "Nephritis," New York, 1912, 113; "Oedema and Nephritis," 3rd ed., New York, 1921, 206, 301, 315, 367, 393, 640

<sup>10</sup> Martin H. Fischer, *Chem. Eng.*, **27**, 272 (1919); "Soaps and Proteins," New York, 1921, 235



from such protoplasm all lie well above this level.<sup>11</sup> The distinction is an important one because the laws of the physical chemists have been discovered, for the most part, upon systems which lie in the upper halves of these diagrams and usually in the single zone of the true solutions, A. In attempting to apply the ordinary laws of physical chemistry (like those of the dilute solutions) to protoplasm it has been assumed that this too is something in the nature of that represented by the zone A. How false is such a conclusion is shown in the single fact that not one of the dilute solution laws holds for any living cell. Protoplasm lies nearer the zone Z and it is the physico-chemical laws governing such systems which are more likely to find unobjectional applicability to protoplasm.

#### THE SYSTEM, WATER-DISSOLVED-IN-X

We purpose now to investigate the system phenol-water which in the two phases, water-dissolved-in-phenol and phenol-dissolved-in-water, gives us in handy laboratory fashion the analogues, respectively, of the zones Z and the zones A of the

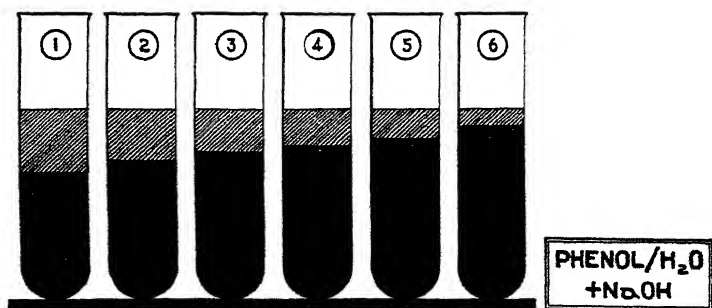


Fig. 2.

diagrams of Fig. 1. Protoplasm is comparable to the solution of the water in the phenol, the secretions from the body to the solution of the phenol in the water. The following paragraphs concern themselves chiefly with the electrical conductivities of these two phases more especially that of the water-dissolved-in-phenol. The significance of these findings for an under-

<sup>11</sup> When protoplasm is "injured" it swells, becomes more liquid, tends to go into better solution in water, shows a higher concentration of materials in molecular solution, etc.—in other words there is a displacement of the protoplasmic system from the lower levels of our diagrams into higher ones.

standing of some of the electrical phenomena observed in protoplasm is returned to later.

Our standard phenol-water systems were prepared by measuring 50 cc. of phenol, liquefied at 50°C., into 100 cc. cylinders and adding 50 cc. of water or the various solutions described in the experiments. After thorough mixing the cylinders were set aside for 18 hours at room temperature. What happens when water only is added is illustrated diagrammatically in the cylinder marked 1 of Fig. 2. It will be observed that two solutions are formed, a lower one of phenol containing water (and usually referred to in the succeeding pages as the hydrated phenol phase) and an upper one of water containing phenol (and usually referred to as the phenolated water phase). After mutual solution has taken place the two phases are unequal in volume. We shall return to this matter later. At 22°C. the phenol phase has a volume of 64 cc., the water phase one of 33 cc. That the sum of the two should not be 100 cc. is explained in part through the contraction of the phenol upon being cooled, in part through the contraction incident to the mutual solution. Our main interest in this paper is in the behavior of the hydrated phenol phase. It should be noted that as water dissolves in the pure phenol its volume increases. The phenol "swells" some 28 to 30 per cent. How this degree of swelling alters under various circumstances and the degree of resistance of the two phases to the passage of an electric current were the main themes of experimental inquiry.

The electrical resistance of the two phases was measured in the customary fashion with a pair of fixed, platinized platinum electrodes of the dip type, by the ordinary Wheatstone bridge arrangement and a telephone. The same electrodes, having the constant .0793, were used in all the experiments, they being repeatedly checked, to show that they had suffered no change, with a 1/50 *N* potassium chloride solution. Since the same electrodes were used throughout, the resistance values are given as observed without calculation in terms of specific resistance. The phenol used was specially purified for us by A. B. Davis by being redistilled in glass in a vacuum (18 mm. Hg) and at a temperature of 112°C. from the highest quality crystallized phenol which the market afforded. It is only such purified phenol which will exhibit the high initial resistances

recorded in the following paragraphs. Our phenol when liquefied at a low temperature and then permitted to crystallize about the electrodes at 22°C. showed a resistance of more than 210,000 ohms. The purest phenol of the open market showed under similar circumstances a resistance of only 2,000 ohms. Such difference is dependent upon the presence of water, neutral salt, dissolved glass and atmospheric gases in the commercial preparation.

The water employed in our experiments was distilled from silver. Freshly obtained it had a resistance of 100,000 ohms. The nature of our experiments was such, however, that we could not protect our ultimate mixtures from air, contamination with carbon dioxide or the effects of our glass containers. Control experiments showed that these circumstances might cut the electrical resistance of our distilled water to 25,000 ohms.

We can sum up the findings of our experiments in the following categorical statements.

1. The electrical resistance of pure phenol is reduced progressively by every increment of water added to it up to its saturation point. From the initial value of 210,000 ohms under the conditions of our experiment (contamination with air and glass), a final resistance of more than 20,000 ohms is registered. We wish now to discover the effects of various electrolytes and non-electrolytes upon the conductivity of this hydrated phenol.

2. When alkali or acid is added to phenol-water the electrical resistance of the hydrated phenol phase falls progressively with every increase in their concentration in the system. Under otherwise similar conditions, alkali reduces the electrical resistance more than acid. From the enormous initial resistance (more than 20,000 ohms) of the pure hydrated phenol the fall is so great between the concentrations of 1/50 to 1/10 *N* HCl (or NaOH) that the ultimate values attained are measurable in two or three hundred for the acid and less than one hundred for the alkali. The resistance of the water phases in equilibrium with these phenol phases is less than 10 ohms in the case of the acid and less than 100 ohms in the case of the alkali.

While both acid and alkali reduce the resistance of hydrated phenol, only the latter markedly influences its volume. While acid seems to decrease it slightly, alkali leads to a progressive

increase in the volume of the phenol phase. The effect is shown in Fig. 2. In common parlance, the phenol "swells" under the influence of the alkali.

3. When employed at the same normality, different alkalies are unequally effective in reducing the electrical resistance of hydrated phenol. Against  $1/25$   $N$  solutions of  $\text{Ca}(\text{OH})_2$ ,  $\text{NaOH}$  and  $\text{KOH}$  the electrical resistances of the phenol phases at  $22.5^\circ\text{C}$ . stand as 303, 280 and 220 ohms. The corresponding water phases register 72, 55 and 46 ohms.

4. The addition of any neutral salt (like sodium chloride or calcium chloride) to a phenol-water system lowers the electrical resistance of the phenol phase. But the nature of the salt employed and its concentration make a difference. At the same normality (from  $1/8$   $N$  to  $2$   $N$ ) sodium chloride reduces the resistance more than calcium chloride (the entire  $\text{NaCl}$  curve lies below the  $\text{CaCl}_2$  curve) while the greatest reduction in resistance of the phenol phase is discovered when the salts are present in a medium concentration.

The volume of the phenol phase, on the other hand, diminishes progressively with every increase in the concentration of either of the added salts.

5. While consideration of the preceding paragraph would by itself indicate that the substitution of calcium chloride for sodium chloride in a phenol-water system would be followed by an increase in electrical resistance, this fact may be demonstrated directly. The resistance of 435 ohms of the phenol phase in contact with a pure  $1/4$   $N$  sodium chloride solution increases progressively to 454 ohms as from 1 to 5 cc. of  $1/4$   $N$   $\text{CaCl}_2$  are substituted in 50 cc. of the original pure sodium chloride solution.

6. At the same molar concentration the decrease in the electrical resistance of hydrated phenol upon the addition of a salt varies with the nature of the acid radical when salts with a common base are compared. While there is a difference even between the individual members of any group the following general statement holds. Univalent acid radicals reduce the electrical resistance of the phenol phase more than do the divalent ones and these more than the trivalent ones. For a series of potassium salts the values in ohms were as follows: sulphocyanate 200; nitrate 300; iodide 306; chlorate 326; brom-

ide 369; chloride 389; oxalate 782; tartrate 881; sulphate 1112; (neutral) phosphate 1087. When salts with a common acid radical are compared, the effects of the bases are found to be different. For a series of chlorides the values were as follows: potassium 377; sodium 594; barium 961; magnesium 1038; calcium 1077; aluminium 1557. Here again divalent radicals are less effective in decreasing the resistance than univalent ones and the trivalent aluminium less than the divalent alkaline earths. The resistances of the water phases were in all cases 7 ohms or less. When compared in equinormal instead of equimolar concentrations the cited differences become still greater. In the concentrations employed the effects of the different salts upon the volume of the phenol phase are too slight to be noteworthy.

7. The addition of increasing amounts of ethyl alcohol at first lowers the electrical resistance of hydrated phenol from over 20,000 ohms to 5,000 ohms and then increases it to twice the original value. While change in resistance thus follows a curve the volume changes are progressive, each increment of alcohol added increasing the volume of the phenol phase. While ethyl alcohol at proper concentration lowers the electrical resistance of hydrated phenol it is less effective in this regard than any of the ordinary electrolytes.

8. Of a series of monatomic alcohols, it is only the lower members which bring about a decrease in the electrical resistance of hydrated phenol. While the hydrated phenol control showed a resistance of 22,000 ohms the addition of 10 cc. of methyl or ethyl alcohol reduced this value to 5204 and 12,123 ohms respectively. Propyl, butyl and amyl alcohols increased the resistance to 27,679, 45,000 and 71,923 ohms. When equimolar amounts of the alcohols are employed instead of equal volumes the described electrical differences are naturally still further exaggerated.

The addition of any of these alcohols leads to increased "swelling" of the phenol phase. It is greatest, however, with the lower members of the alcohol series.

#### COMMENTS

We have no desire to enter at this time upon any detailed discussion of the nature of the causes for the electrical changes

which are observed in the experiments which have been described. This would involve us in a debate regarding the fundamental nature of conductivity in solutions which we wish to avoid. The following facts, however, deserve emphasis.

It is clear that phenol and water yield at least two types of true solution. The broadly accepted view of the physical chemists that their molecular dispersions of one material in a second are always to be thought of as systems of one type only needs therefore to be revised. Since the two phases will not mix excepting to form a frank emulsion, it follows as a matter of necessity that the solution of phenol in water has a structure definitely different from that of water in phenol. The solution of phenol in water is the one upon which physical chemists have bestowed chief study. It is the second type of solution, however, which bears the closer analogy to living matter and it is therefore the physical chemistry of this system which we may expect to find more directly applicable to protoplasm. We wish to suggest, however, that their physical chemistry may also serve to explain much of the "exceptional" behavior which the "true" solutions show when concentrated, for example. As such concentration takes place, materials having the structure solvent-dissolved-in-dissolved-substance must appear in increasing amount and in this proportion modify linear laws characteristic of the classical "dilute" solutions.

The findings described in the preceding paragraphs indicate also that several factors need to be considered when any interpretation of the electrical changes observed is attempted. When acid or alkali is added to hydrated phenol there is a decrease in the electrical resistance just as when acid or alkali is added to water. This observation might be interpreted as the direct consequence of solution of the electrolyte in the hydrated phenol with secondary electrolytic dissociation of the dissolved materials as in the case of pure water. Something more, however, happens in the hydrated phenol to disturb this simple picture. While the addition of acid does not markedly influence the volume of the hydrated phenol phase, addition of alkali enormously increases its water-holding capacity.

In the case of the neutral salts, reduction in the electrical resistance might again be conceived of as due to solution of the salts in the hydrated phenol and ionization. Their less ready

solubility and lower degree of ionization in this medium might then be used to explain the lesser effects of trivalent salts as compared with divalent ones and these as compared with univalent ones. This simple idea is also disturbed if the hydrated phenol is investigated when in equilibrium with an aqueous solution of the electrolyte. With ascending concentration of the latter the water-holding power of the hydrated phenol is increasingly diminished. Obviously, a final answer to the qualitative and quantitative nature of the various changes involved will require analyses directed to the distribution of water, phenol and electrolyte in the two phases and their volumes.

The effects of the alcohols suggest further interesting problems. In spite of their classification as non-electrolytes the lower alcohols bring about some decrease in electrical resistance when added to water-phenol systems. With progressive additions, however, the resistance of the hydrated phenol rises and this is accomplished in spite of a progressive increase in the volume of the hydrated phenol. To understand the latter fact, in such apparent contradiction to the behavior of the salts, it will be necessary, we think, to have recourse to an opinion expressed before, that, namely, even the true solution represents more than a molecular dispersion of one material in a second. There is, in addition, union with solvent.<sup>12</sup> When a salt solution covers the hydrated phenol phase the salt particles may unite with the water and so abstract it from the hydrated phenol and thus diminish the volume of the latter. In the case of alcohol, there is possible a similar union with water, but the tendency of the alcohol to unite with the phenol, especially in the case of the higher alcohols, is even greater.

#### BIOLOGICAL REMARKS

1. We wish now to comment briefly upon the significance of the experiments described above for a better understanding of certain aspects of cell behavior. For many years past the question of the "permeability" of "cell membranes" and more recently of "protoplasm" in general has been the subject of

<sup>12</sup> It needs constantly to be borne in mind that such hydration (or solvation in general) may also be of at least two kinds. The water united to a neutral salt in the ordinary salt solution, for example, is combined with this as is the water of any of the soaps when soap dissolves in water. The form of this union is different from that when the water dissolves in the soap

extensive experimental inquiry and debate. It is unnecessary to enter into detailed discussion of the physico-chemical and biological deductions to which these have given rise. Such may be found in the papers and texts of E. Overton,<sup>13</sup> H. J. Hamburger,<sup>14</sup> Rudolph Höber,<sup>15</sup> J. F. McClendon,<sup>16</sup> E. Newton Harvey,<sup>17</sup> W. J. V. Osterhout<sup>18</sup> and others. No one can attempt a critical analysis of such studies without a feeling of dismay. In spite of many contradictions both in observed facts and deductions some fundamental harmonies, however, remain.

The first permeability studies were built upon the osmotic concept of the living cell as originally defended by Pfeffer and De Vries. The living cell was, according to their notion, a sacule of fluid encompassed by a semi-permeable membrane, a membrane, in other words, impermeable to all dissolved substances but readily permeable to water. This concept showed early both physico-chemical and biological shortcomings. A first observation of a disturbing type was made by these authors themselves when they noted that various dissolved substances would diffuse into cells and precipitate the tannin contained therein. Later studies then revealed that no living cell could be found which would obey the physico-chemical laws of osmotic pressure. But from a biological point of view this could prove even less adequate for how, on an osmotic basis, while capable of volume change through migration of water into or out of it, could it take up dissolved foods or rid itself of dissolved metabolic products? Upon such grounds we early denied the existence of semi-permeable membranes about living cells.<sup>19</sup> Those who continued to adhere to the osmotic concept of the

<sup>13</sup> E. Overton, *Vierteljahrsschr. Naturforsch. Ges. Zurich*, **40**, 1 (1895); *ibid.*, **44**, 88 (1899); *Z. physik. Chem.*, **22**, 189 (1897); *Pflüger's Arch.*, **92**, 115 (1902); *ibid.*, **92**, 261 (1902); Nagel's "Handbuch d. Physiol.," **2**, 2te Hälfte, 744 (1907)

<sup>14</sup> H. J. Hamburger, "Osmotischer Druck und Ionenlehre," **1**, 202, Wiesbaden (1902)

<sup>15</sup> R. Höber, "Physikal. Chem. d. Zelle und d. Gewebe," 5te Aufl., 367 and 404, Leipzig (1922) as well as the older editions

<sup>16</sup> J. F. McClendon, *Pop. Science Monthly*, 568 (1915); *Am. J. Physiol.*, **38**, 163 (1915); *ibid.*, **38**, 173 (1915); *Am. J. Surg.*, Anesthesia Supplement, **35**, 104 (1921)

<sup>17</sup> E. Newton Harvey, Yearbook No. 10, Carnegie Institution, 1910, 128; *J. Exp. Zool.*, **10**, 507 (1911); *Am. J. Physiol.*, **31**, 335 (1913)

<sup>18</sup> W. J. V. Osterhout, "Injury, Recovery and Death," Philadelphia, 1922

<sup>19</sup> Martin H. Fischer, *Am. J. Physiol.*, **20**, 330 (1907); *Pflüger's Arch.*, **124**, 69 (1908); *ibid.*, **125**, 99 (1908), *ibid.*, **127**, 1 (1909); *ibid.*, **127**, 46 (1909); "Oedema," New York, 1910



living cell have met the difficulties of the situation by making the original osmotic membrane of Pfeffer and De Vries partially permeable to at least certain dissolved substances or bestowing upon this membrane special characteristics (like the lipid composition of Overton). We have often enough showed the inadequacy of both of these modifications. To make the membrane permeable to dissolved substances is to destroy to this degree the possibility of moving water through concentration differences of the dissolved substances; while the substitution of a lipid membrane about the cells for the older osmotic one, though helping toward an explanation of the absorption of fat-soluble materials, make impossible the absorption or secretion of salts, water, etc. *The living cell is capable of absorbing and secreting water and of absorbing and secreting the most varied types of dissolved materials, the two moving at times in the same direction and at times in opposite directions. There can be no adequate physico-chemical concept of the living cell which does not contain within it the possibility of understanding all these characteristics of the living cell at one and the same time.*

We have repeatedly emphasized that the hydrophilic colloid (especially one protein in nature, like a particle of fibrin) is possessed of all the powers of taking up and giving off water shown by the living cell under various conditions while it has at the same time all the powers of taking up and giving off dissolved substances which are characteristic of living matter. All this occurs, of course, without the need of assuming that the hydrated colloid mass has a membrane about it which differs in any way from the rest of the fibrin flake. Our more recent studies<sup>20</sup> have shown that such a protein mass, combined with acids and alkalis or salts and saturated with water (and comparable in this form with the foundation material constituting the cell) is in essence a system comparable to water-dissolved-in-phenol. It is this water-dissolved-in-phenol system which when subjected to the action of alkalis or of salts "swells" and "shrinks," shows in other words the biological phenomena of plasmolysis and plasmolysis (too commonly still explained on an "osmotic" basis) just as does a hydrophilic colloid (a

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<sup>20</sup> Martin H. Fischer, *Science*, **48**, 143 (1918); "Soaps and Proteins," New York. 1921, 205

protein) or a living cell. But this system shows also the "strange" phenomena of "permeability" to dissolved substances so characteristic of living matter. When phenolated water and hydrated phenol are in contact with each other the latter phase will take up certain substances better than the former or *vice versa*. And here the analogy to what has been observed in permeability studies on living cells is again great. The hydrated phenol is quickly "permeable" to the most varied dyes (Nile blue sulphate, neutral red, methyl red, methyl violet, methyl green) and will practically exhaust the water phase in a few hours. Other substances (like eosin or iodine) will pass in less quickly and less completely. All the salts (so often held by various biological students incapable of entering or leaving the uninjured living cell) enter the hydrated phenol phase either very slowly or not at all. Ferric chloride, cupric acetate, cerium sulphate (or their hydrolytic products) all enter the phenol phase but with decreasing facility; chromium chloride, chromium sulphate, cobaltous chloride, nickel chloride seem to remain entirely in the aqueous phase. Of "colloid" substances, infusorial earth concentrates in the aqueous phase, boneblack in the phenol phase.<sup>21</sup>

2. The experiments described above were devised to show, if possible, that the peculiarities which living matter shows toward the passage of an electric current through it may also be readily understood as soon as it is remembered that the cell is not, as so long conceived, a dilute solution of x-in-water but one of water-in-x, comparable to the system water-in-phenol.

The first fact which strikes the student investigating the electrical resistance of cells or biological fluids is its height.<sup>22</sup> In spite of the conclusion that a "physiological" salt solution (say a 0.7% or 0.9% NaCl) is supposed to be "osmotically" comparable with that of the salts "dissolved" within the ordinary living animal cell or its fluid, the former will register, with a standard pair of electrodes, only 1/5 to 1/35 the electrical resistance of uninjured cells, muscle juice, lymph, blood, egg

<sup>21</sup> We hope to return to this observation later in connection with the question of phagocytosis

<sup>22</sup> See the many observations covering this point beginning with W. Roth, *Zentr. Physiol.*, 11, 271 (1897); Bugarszky and Tangl, *ibid.*, 11, 297 (1897); *Pflüger's Arch.*, 72, 531 (1898); G. N. Stewart, *Zentr. f. Physiol.*, 11, 332 (1897); *J. Physiol.*, 24, 356 (1899); *Am. J. Physiol.*, 49, 233 (1919)

white or egg yolk. This old biological truth can be understood only by denying to the salts found in protoplasm any large existence in uncombined form<sup>23</sup> or by concluding that the cell is a different sort of solvent for these salts than is water. Experimental facts, we think, support both these conclusions. The high electrical resistance characteristic of living protoplasm cannot be observed in solutions of the type phenol-dissolved-in-water but in those of the type water-dissolved-in-phenol.

When it comes to the changes in electrical resistance evidenced by living cells when subjected to intoxication, injury or environmental change, the following findings are noted by all observers. Through the action of acids or alkalies, the electrical resistance of protoplasm is reduced. In similar fashion acids and alkalies are most powerful in decreasing the electrical resistance of hydrated phenol. But potassium hydroxide affects protoplasm more than equally concentrated sodium hydroxide and this than calcium hydroxide. Hydrated phenol behaves similarly. Solutions of single salts also reduce the electrical resistance of living cells but are less effective in this regard than the acids or alkalies. This is characteristic, too, of hydrated phenol. A single salt when acting upon a cell may, however, show a lack of uniformity in this regard, at certain concentrations proving more effective than at others. This, too, is seen in the curves illustrating the behavior of hydrated phenol. The absolute differences in physiological effect exhibited by different salts when employed in comparable concentrations is also repeated in the case of hydrated phenol. Finally, the physiological antagonism between different salts (the ability of a divalent radical, for example, to counteract the reducing effects of a univalent one) may also be observed upon hydrated phenol. Even the effects of certain non-electrolytes in reducing the electrical resistance of protoplasm (as that of the anesthetic alcohols) may be rediscovered in hydrated phenol systems.

What has been said for phenol-water systems is true of many other mutually soluble systems. Quinoline, for example, behaves much like phenol and what has been said of these substances holds also for the lower fatty acids, the soaps and the various proteins.

<sup>23</sup> See in this connection Martin H. Fischer, "Soaps and Proteins," New York, 1921, 228

## SUMMARY

After a discussion of the theory of the colloid state in which the lyophilic colloid is defined as the product of two mutually soluble substances and is placed in parallel with the behavior of systems represented by phenol-water, the phase represented by the solution of water in phenol (hydrated phenol) is given special study. It is this phase which is regarded as comparable to protoplasm and its physico-chemical characteristics are held to be those important for an understanding of the properties of living matter.

Pure hydrated phenol has a very high electrical resistance. This is reduced through the addition of acids or alkalies. It is also reduced through the addition of various neutral salts but less markedly. For all these substances, the degree of reduction is dependent not only upon the concentration of the material added, but also upon the nature of the acid or basic radicals present in the compound. Since salts, for example, are unequally effective at the same concentration in reducing the electrical resistance of hydrated phenol, it is easy to demonstrate an "antagonism" between them. Certain non-electrolytes, like the lower alcohols, also reduce the electrical resistance of hydrated phenol though not as much as do the electrolytes.

This behavior of hydrated phenol parallels the behavior of cells and body fluids when exposed to similar conditions.

The presence of various electrolytes or non-electrolytes in phenol-water mixtures changes also the volume assumed by the hydrated phenol phase. While various acids slightly decrease the volume, alkalies markedly increase it (they make the phenol "swell"). Salts diminish the volume of hydrated phenol and in increasing amount with increase in their concentration.

Such behavior, too, parallels water absorption and water loss as observed in living cells, so commonly attributed to variations in their "osmotic pressure."

The fundamental error of considering protoplasm as something comparable to a dilute solution is reemphasized. It is essentially not a solution of protoplasmic material dissolved in water (like phenol-in-water) but one of reverse type, namely, water dissolved in protoplasmic material (like water-in-phenol).

It is the physico-chemical laws which govern the latter type of system which reappear in living matter.

DISCUSSION ON M. H. FISCHER'S PAPER

THE THEORY OF THE LYOPHILIC COLLOIDS

H. S. TAYLOR: I think a vote of congratulation is in order to Dr. Fischer because he has made a very brilliant discovery. He has discovered some of the fundamentals we have been looking for. This discovery was made because Dr. Fischer went out of his way to do something. I think we have to admit that all the new apparatus which is being placed at our disposal, which for example Prof. Svedberg laid down for us so beautifully the other afternoon, is bringing us further than is possible by the old methods. I used to go to the market place as a boy and used to derive a lot of enjoyment from the observations of the people selling herbs, but now I find no time for a man selling herbs but I would like to know all about the individual who has been the most up-to-date scientific man, so scientific that he makes use of all the latest experimental apparatus. Therefore I think the attitude of mind which tends to despise these instruments isn't a correct attitude of mind.

E. B. SPEAR: I hope the remarks by any speaker will not be taken too seriously. I think that would be a great mistake. We are using instruments and so is Dr. Fischer and he enjoys it as much as we do. I would like to call attention to a term that is used in colloid chemistry, and in chemistry in general, namely, hysteresis.

I do not know whether I misunderstood Dr. Fischer this morning with regard to the last part here (indicating on board). With respect to this picture that he has before us, he said that we have a reversal of phase in which the dispersion medium is soap-water, and so forth; I do not believe Dr. Fischer means that. What I think we have is a dispersion medium of soap-water but inside we have particles of water, not pure water but saturated solution.

J. H. MATHEWS: As a physical chemist I was rather surprised to hear you say, Dr. Fischer, that up at the top here (indicating on diagram) you have a true solution that shows a normal osmotic pressure and normal freezing and all that,

and does not exhibit colloidal effects. The fact that it shows a well-defined Tyndall cone would seem to prove that we were dealing there with a colloidal system.

VOICE: On two occasions now I have heard the statement made that plant physiologists used to teach that the protoplasm was entirely out of joint in this connection. I heard that made last winter and again this morning by Dr. Fischer. In all of my experience as a student of physiology I never had that idea given to me as a student of physiology. I do not know where these people get that idea. It seems to me that the statements they make are far reaching.

M. H. FISCHER: It is a ridiculous charge to say that I am claiming to have discovered the distribution law of Berthelot and Jungfleisch. No one who has ever read one of my articles or books could make it. As a physiologist I have for many years emphasized its importance for an understanding of many of the "strange" phenomena observed in "selective absorption and secretion." In my remarks just now I again point out that the inequalities in distribution of any soluble material between a hydrated phenol phase and a phenolated aqueous phase are like the inequalities observable, for example, between our cells and aqueous secretions from such cells, like the urine. My "discovery" lies in my insistence that the cells are comparable to the hydrated phenol phase and not, as the physical chemists and physiologists have too long taught, to a dilute aqueous solution like the phenolated water. It is also ridiculous to charge that I disparage progress in the building of apparatus and the refinement of quantitative studies. What I object to is the misapplication of such things. Internal medicine has been called upon to witness. It is a field in which I am supposed to be at home so I may be specific. We are teaching our new men how to make basal metabolism determinations, electrocardiographs and hydrogen ion determinations on every fluid of the body. I do not object to these things as aids to older methods but I consider them poor substitutes for the older practices of seeing with the eyes, hearing with the ears and feeling with the fingers. The factor which expresses the exception to a law is not as important, in my mind, as the law itself.

The statement regarding hysteresis is proper. I used the term as synonymous with lag. To argue the state of the salts in the cells would take us too far afield, but the mere fact that the conductivity of protoplasm is far below that of an equal volume of water containing the physiological concentration of salt, is, I think, definite proof that something has happened to the salt; it must either have combined with something in the cell or else protoplasm is a different solvent for the salt than is water. I would like in this connection to mention the name of a man too little known to American science although I esteem him one of our greatest. I refer to John Uri Lloyd. He believes that not even the alkaloids exist as such in normal uninjured plants. He has analyzed the "dew," for instance found upon alkaloid bearing plants. Aside from the fact that the "dew," is commonly not dew at all but an aqueous secretion from the plant, he never found it to contain alkaloids.

The question of the soaps I need not go into. I am content to admit that the higher soaps at least never form true solutions. It is the physical chemists, like McBain, who have consistently maintained that they do, up to a few years ago. Dr. Spear is right in saying that in the lower portions of my diagrams the internal phase is not pure water but a saturated solution of the soap in water.

The question was raised as to who of the plant physiologists it was that maintained that cells were impermeable to salts. Overton held to that view and Höber, the animal physiologist, believed it so firmly that he claimed the salts from the alimentary tract to be absorbable only by way of the intercellular substances.

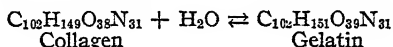
[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

## CONDITIONS AFFECTING THE HYDROLYSIS OF COLLAGEN TO GELATIN

BY ROBERT H. BOGUE

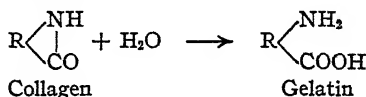
### INTRODUCTION

There has been but little work reported dealing with the hydrolysis of collagen. Hofmeister<sup>1</sup> as far back as 1878 regarded the change of collagen to gelatin as a simple hydration, one molecule of water being added to each molecule of collagen:



He regarded collagen, therefore, as a simple anhydrid of gelatin, and considered the reaction as reversible since, on heating the gelatin to 130°C., he believed he obtained a regeneration of the collagen. This material was much less soluble than gelatin, but Alexander<sup>2</sup> and also Emmett and Gies<sup>3</sup> have contended that the conversion of collagen to gelatin was more complex and not reversible. The latter investigators found that whereas collagen was not attacked by trypsin, yet normal gelatin and also dehydrated (at 130°C.) gelatin were readily attacked by that enzyme. They also reported that ammonia was evolved upon heating collagen in water, while this did not occur upon a similar treatment of gelatin.

Plimmer<sup>4</sup> believes that the difference in the action of pepsin and trypsin lies in the ability of the former, and the inability of the latter, to open up an anhydrid ring. He thinks that all proteins which are resistant to the action of trypsin until they have been acted upon by pepsin "have all their units contained in the anhydrid ring." Thus the conversion of collagen to gelatin might be represented:



<sup>1</sup> F. Hofmeister, *Z. physiol. Chem.*, **2**, 299 (1878)

<sup>2</sup> J. Alexander, Allens' "Commercial Organic Analysis," **8**, 586 (1913)

<sup>3</sup> A. Emmett and N. Gies, *J. Biol. Chem.*, **3**, XXXIII (1907)

<sup>4</sup> R. Plimmer, "Chemical Constitution of the Proteids," 2nd ed., Part II, 1912, p.11



The present investigation was undertaken in the hope that further light might be found which would indicate the nature of the conversion into gelatin, and more particularly to study the several conditions affecting the hydrolysis. The following influences were examined in this investigation:

Hydrogen ion concentration	Ratio of stock to water
Presence of salts	Agitation
Temperature	Condition of stock
Duration of heating	The plumping reagent.

The procedure adopted involved an hydrolysis in water or other electrolyte for a definite period at a definite temperature. The distribution of the nitrogen between that recovered in the solution, that evolved as ammonia during hydrolysis, and that remaining in the residue was determined. The amino nitrogen was determined as one means of checking the extent to which the gelatin molecule had been degraded during the hydrolysis. The H ion concentration was determined electrometrically in the solution. The viscosity and jelly consistency were also determined as further checks on the degree of hydrolysis that had taken place.

#### EXPERIMENTAL PART

The stock used throughout the greater part of these experiments was well-limed hide pieces. The liming had been carried out at the glue factory in the usual way by soaking the hide cuttings in milk of lime, with occasional changes, for about ten weeks. It was kept in the cooler and used as required. Except as especially noted below, the stock, preparatory to use, was washed several times in water at about 15°C. until all dirt, hair, and lime that could be removed had been freed from the stock. The fatty portions on the inner surface were removed and the trimmings cut into uniformly sized pieces of about  $2 \times \frac{1}{2} \times \frac{1}{2}$  inches. These were then ready for the hydrolysis. The water content and the total nitrogen by a modified Kjeldahl method were determined as these values were necessary for the final calculations.

The basic procedure in the hydrolysis was as follows:

Five hundred grams of stock prepared as above were weighed into a 2 liter flask and 800 cc. of distilled water (or other solution) at 80°C. added. The flask was at once placed in a water-

oil thermostat regulated to a temperature of  $80^{\circ}\text{C}.$   $\pm 0.1^{\circ}$ . Air, purified by passing through a solution of potassium hydroxide, and saturated with water by passing through water at  $80^{\circ}\text{C}.$ , was caused to bubble slowly through the flask and then passed through a measured quantity of standard  $N/10$  hydrochloric acid. By a subsequent titration, any ammonia evolved during the hydrolysis was determined. The flask was allowed to remain undisturbed for exactly 8 hours at the end of which period the solution was strained through a 100 mesh sieve, and put in the cooler until the following day. The residue was in some cases examined for water and nitrogen content to find the nitrogen unrecovered, but this procedure was found to check that found by difference between 100 and the nitrogen recovered in solution plus the nitrogen evolved as ammonia, and so was discarded.

The solution was placed in a water thermostat regulated to  $35^{\circ}\text{C}.$   $\pm 0.03^{\circ}$  and all measurements made at that temperature. The total nitrogen of the solution was determined by a modified Kjeldahl method, and recorded as percentage of the total nitrogen of the original stock recovered in solution. The amino acid nitrogen was determined by both the nitrous acid method of Van Slyke<sup>5</sup> and the formaldehyde titration method of Sørensen.<sup>6</sup> The former method gave results a little higher than the latter in most instances.

The hydrogen ion concentration was determined by the use of the hydrogen electrode, using the apparatus of Clark<sup>7</sup> and a  $N/10$  potassium chloride calomel half cell. A Leeds and Northrup type K potentiometer was employed.

The viscosity was measured at  $35^{\circ}$  by means of an Ostwald capillary-tube viscosimeter, and expressed as seconds of outflow. (Since relative results only were desired.) The jelly consistency was measured by an improvised instrument of the Lipowitz<sup>8</sup> type. The solution was placed in a closed jar  $4 \times 1.5$  inches, and set in the cooler at  $5^{\circ}\text{C}.$  for 24 hours. The pressure

<sup>5</sup> D. D. Van Slyke, *J. Biol. Chem.*, **9**, 185 (1911); **12**, 275 (1912); **16**, 121 (1913); **23**, 407 (1915)

<sup>6</sup> S. Sørensen, *Biochem. Z.*, **7**, 45 (1908)

<sup>7</sup> W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1920, p. 129

<sup>8</sup> See R. H. Bogue, "Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., New York, 1922, pp. 371-2

necessary to force a  $\frac{3}{8}$  inch glass rod through the surface was measured and this expressed as grams.

#### VARYING HYDROGEN ION CONCENTRATION

In the first series the solutions added to the stock consisted of dilute hydrochloric acid, water, and sodium hydroxide of such concentrations that the final solution as recovered varied in H ion concentration from  $p_H$  0.1 to  $p_H$  12.4. About 35 runs were made, so that the interval in  $p_H$  between different runs was in all cases slight.

The data obtained are shown in Tables I and II.

In Figs. 1 to 5 are plotted the curves for the several columns of data taken from Table II. In each case the  $p_H$  is indicated on the abscissa. The ordinates represent, in Fig. 1, the

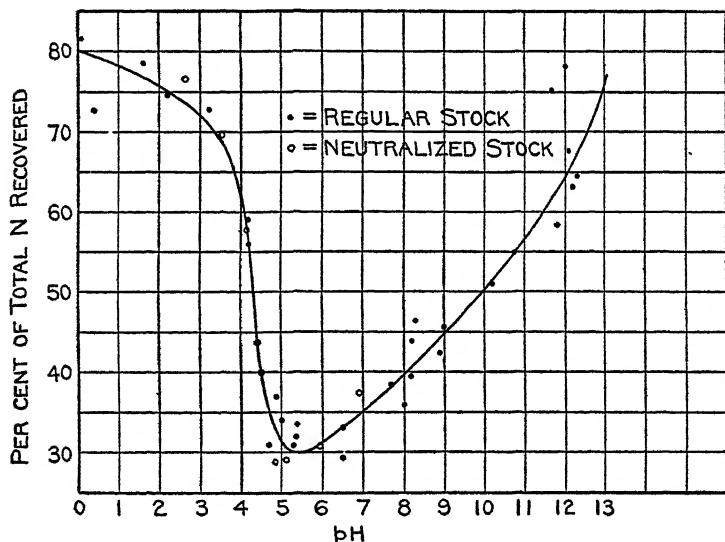


FIGURE 1

EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF THE TOTAL NITROGEN RECOVERED IN THE SOLUTION

percentage of the total nitrogen recovered in the solution; in Fig. 2, the percentage of the total nitrogen evolved as ammonia; in Fig. 3, the percentage of the nitrogen of the solution which is in the form of terminal amino groups; in

TABLE I  
WATER AND NITROGEN CONTENT OF PREPARED STOCK

Water in prepared stock		Nitrogen in dried stock	
Per cent.		Per cent.	
80.70		14.13	
78.00		14.00	
80.50		14.26	
81.19		14.10	
80.35		13.23	
80.65		14.58	
.....		14.22	
Average	80.23	Average	14.07

Fig. 4, the viscosity of the solution at 35°C. expressed in seconds of outflow through an Ostwald viscosimeter; and in Fig. 5, the jelly strength at 5°C. in grams.

The tables and figures bring out a few points which should be emphasized. In the first place, there is a great deal of

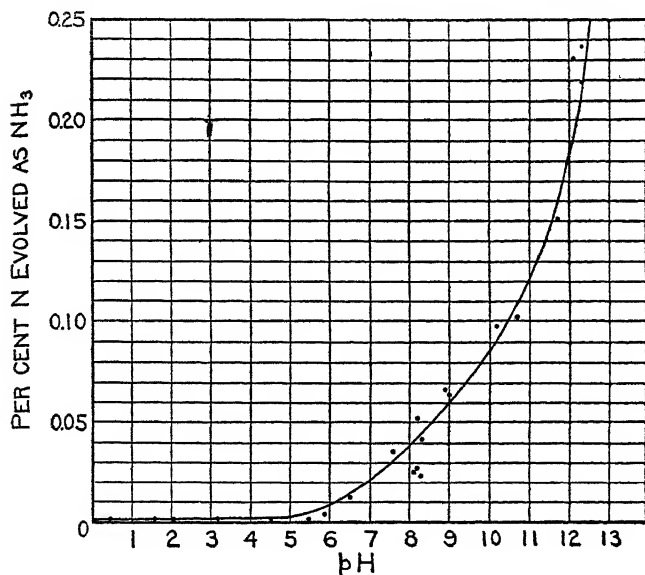


FIGURE 2

EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF NITROGEN EVOLVED AS NH<sub>3</sub>

TABLE II  
HYDROLYSIS DATA AT VARYING H ION CONCENTRATIONS

Hydrolyzing solution	Volume of solution recovered	Total N in solution	Amino N in solution	NH <sub>3</sub> evolved	N in residue	Viscosity	Gel strength	$\bar{p}_H$
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Sec- onds	Grams	
0.5 N HCl	1280	81.88	10.29	0.001	18.12	104	Liquid	0.1
0.5 N HCl	1290	72.68	11.32	0.002	27.32	95	Liquid	0.4
0.35 N HCl	1250	78.50	11.50	0.001	21.95	112	10	1.6
0.30 N HCl	1250	74.55	9.61	0.001	25.95	120	10	2.1
0.250 N HCl	1220	72.74	6.38	0.001	27.26	150	20	3.2
0.152 N HCl	1000	59.07	8.13	.....	40.93	237	20.5	4.2
0.152 N HCl	1000	55.99	9.18	.....	44.01	209	20.5	4.2
0.145 N HCl	1000	40	5.12	0.001	60	162	26	4.5
0.145 N HCl	1000	31.06	3.38	0.002	68.94	120	15	4.7
0.131 N HCl	1000	34.00	4.56	.....	66	138	25	5.0
0.112 N HCl	1000	30.8	4.1	.....	69.2	170	31	5.3
0.112 N HCl	1000	30.1	4.1	0.001	69.9	176	32	5.3
0.131 N HCl	1000	32	4.1	0.001	68	154	28	5.4
0.10 N HCl	1000	33.71	6.79	0.001	66.29	194	44.7	5.4
0.10 N HCl	1000	36.97	6.43	0.005	63.02	189	48.9	5.9
0.045 N HCl	1000	29.56	4	.....	70.44	210	50	6.5
0.045 N HCl	1000	33.22	3.9	0.012	66.77	201	55	6.5
0.051 N HCl	1000	.....	.....	0.035	.....	336	66.2	7.6
0.051 N HCl	1000	.....	7.74	.....	.....	386	79.9	7.7
H <sub>2</sub> O	1000	38.24	6.56	.....	61.76	266	67.8	7.7
H <sub>2</sub> O	1000	45.22	6.27	0.025	54.76	315	.....	8.1
H <sub>2</sub> O	1000	59.36	5.77	0.052	40.59	461	70.9	8.2
H <sub>2</sub> O	1000	43.6	3.12	0.026	56.37	207	80	8.2
H <sub>2</sub> O	1000	46.4	3.07	0.023	53.58	214	85	8.3
H <sub>2</sub> O	1000	39.53	6.19	0.041	60.43	262	.....	8.3
0.1 N NaOH	1000	42.80	8	0.066	57.13	160	30	8.9
0.1 N NaOH	1000	45.52	8	0.064	54.42	175	35	9.0
0.20 N NaOH	1240	51	14.7	0.098	48.9	115	10	10.2
0.20 N NaOH	1220	55.1	13.8	0.102	44.8	114	10	10.7
0.249 N NaOH	1275	75.20	23.21	0.150	24.65	84	Liquid	11.7
0.249 N NaOH	1265	58.60	24.10	0.072	41.33	79	Liquid	11.9
0.467 N NaOH	1270	78.33	30.31	0.231	21.44	83	Liquid	12.1
0.467 N NaOH	1255	67.64	36.06	0.333	32.03	82	Liquid	12.1
0.5 N NaOH	1280	64.74	41.24	0.236	35.02	79	Liquid	12.3
0.5 N NaOH	1270	63.51	47.94	0.219	36.27	81	Liquid	12.3

fluctuation from the mean curves which may be drawn from the data. A single test at any point means very little and it is only by the accumulation of a considerable number of analyses that we are permitted to draw representative curves. This is due to the irregularity, in spite of care in selection, of the stock employed, and of its water and nitrogen content. But from the large number of data in hand we are justified in making specific conclusions.

Fig. 1 shows that when the concentration of acid in the

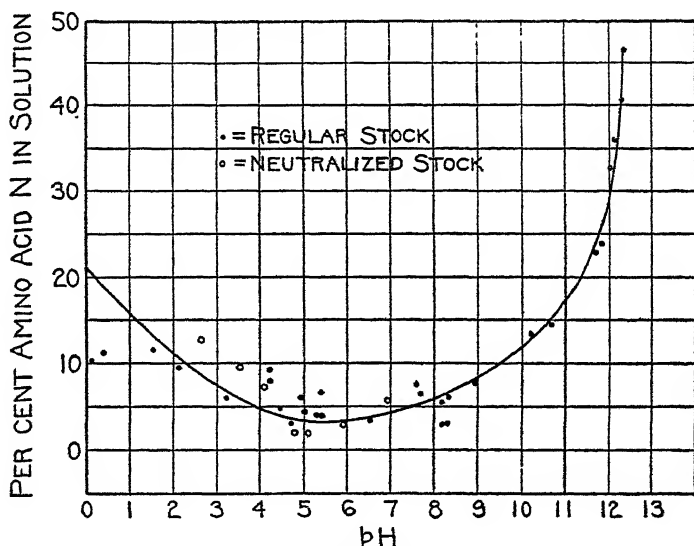


FIGURE 3

EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF AMINO ACID NITROGEN RECOVERED IN THE SOLUTION.

hydrolyzing mixture is such as to bring the acidity of the final solution to about  $p_H$  5 or 6, the hydrolysis is least, only about 30 per cent. of the nitrogen of the stock passing into solution under the conditions of the experiment. At slightly stronger concentrations of acid the hydrolysis increases markedly, and it also increases, but less rapidly, with increasing alkalinity.

Fig. 2 shows that up to a  $p_H$  of 5.4 there is practically no evolution of ammonia, as of course would be expected, but that

above  $p_H$  5.4 ammonia is evolved in amounts increasing rapidly with the alkalinity of the solution.

Fig. 3, indicates the extent of the secondary hydrolysis, namely the breaking down of the gelatin molecule into its degradation products: proteose, peptone and amino acids. Throughout the range of  $p_H$  3 to 8 this secondary hydrolysis is slight, but beyond either of these limits, and especially at moderately high alkaline concentrations, as  $p_H$  12, it becomes very important.

The variation in viscosity with  $p_H$  of hydrolyzing solution

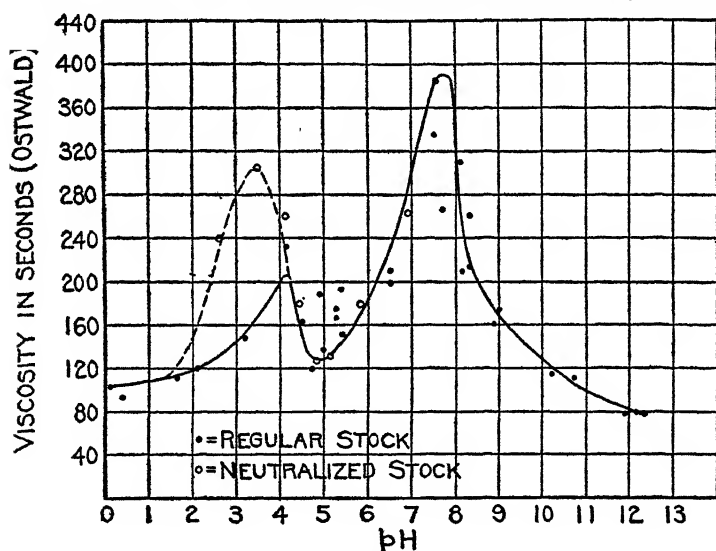


FIGURE 4

EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON VISCOSITY OF PRODUCT AT 35°C

is shown in Fig. 4. There is indicated a distinct minimum at  $p_H$  4.5 to 5.0 and a maximum at  $p_H$  7.5 to 8.0. There is also a lesser high point at  $p_H$  4.1.

The jelly strength curve shown in Fig. 5 is very similar to the viscosity curve.

#### INFLUENCE OF SALTS

It seemed possible that the excess of lime which remained in the stock after the washing as usually carried out might

influence the results, and a number of runs were made following a special preliminary treatment. The stock was first washed a number of times with cold water, and then placed in a ball mill with a solution of hydrochloric acid of about  $N/100$ .

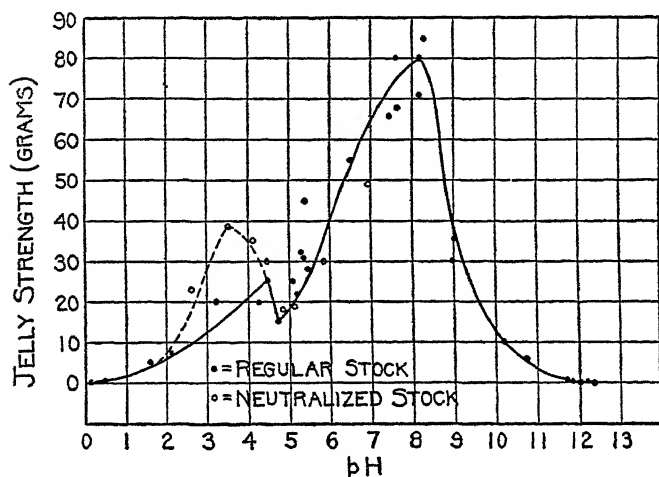


FIGURE 5

EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON JELLY STRENGTH OF PRODUCT AT 10°C

This washing was followed again by a washing in water. This left the stock practically neutral as shown by the fact that an hydrolysis in pure water gave a final solution of  $p_H$  6.9.

Different amounts of concentrated hydrochloric acid were

TABLE III

HYDROLYSIS DATA ON NEUTRALIZED STOCK

Hydrolyzing solution	Volume of solution recovered	Total N in solution	Amino N in solution	N in residue	Viscosity	Gel strength	$p_H$
	Per cent	Per cent.	Per cent	Per cent.	Seconds	Grams	
0.2 N HCl	1200	76.8	12.7	23.2	239	23	2.6
0.17 N HCl	1120	69.6	9.4	30.4	303	39	3.5
0.13 N HCl	1000	58.0	7.5	42.0	261	35	4.1
0.1 N HCl	1000	44.2	5.0	55.8	180	30	4.4
0.08 N HCl	970	29.0	2.1	71.0	128	18	4.8
0.07 N HCl	975	29.3	2.2	70.7	132	19	5.1
0.05 N HCl	990	30.9	3.0	69.1	180	30	5.8
H <sub>2</sub> O	1050	37.5	5.9	62.5	265	49	6.9



then introduced into the hydrolyzing solution and runs made as before. There was no observable variation in the resulting data until the acidity of the final solution showed a  $p_H$  of about 4.1. From  $p_H$  4.1 to  $p_H$  2.6 the solution showed a higher vis-

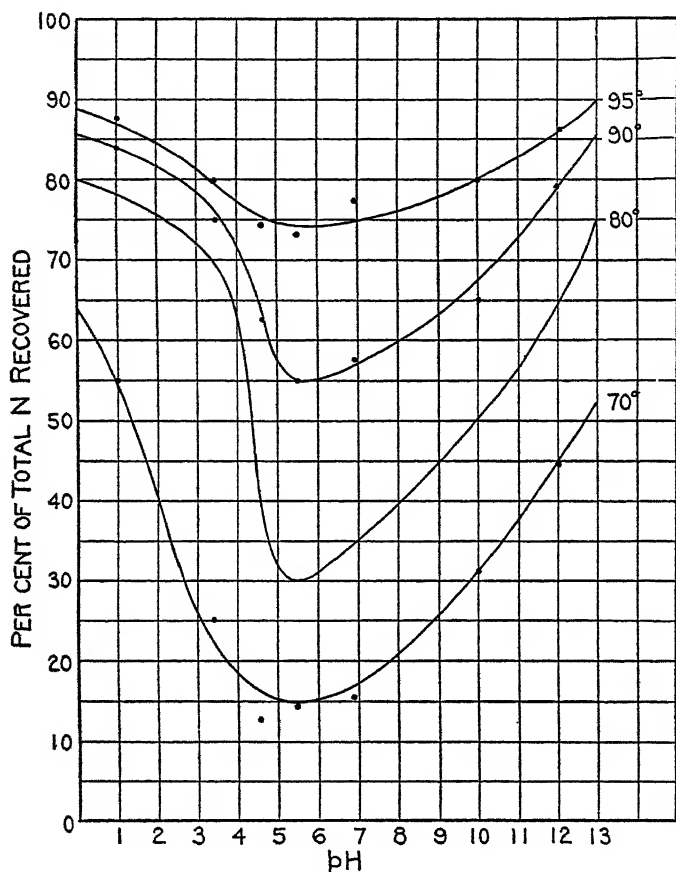


FIGURE 6

INFLUENCE OF TEMPERATURE ON TOTAL N RECOVERED  
IN THE SOLUTION AT VARYING  $p_H$

cosity and jelly strength than the previous tests of similar acidity, but the amount of nitrogen recovered and the degree of the secondary hydrolysis were not noticeably altered. Ammonia was not determined in this series.

The data are given in Table III, and the differences in the curves for viscosity and jelly strength are shown by the dotted lines in Figs. 4 and 5.

#### INFLUENCE OF TEMPERATURE

Having established the general direction and nature of the several curves illustrative of the hydrolysis, it seemed very

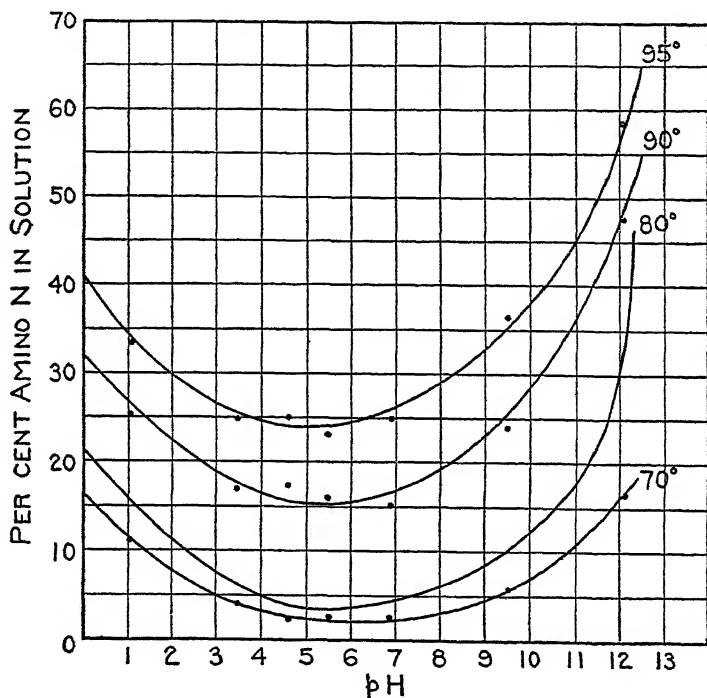


FIGURE 7  
EFFECT OF TEMPERATURE ON AMINO N IN THE  
SOLUTION AT VARYING pH

desirable to determine the influence which a number of other factors exerted in the process. The influence of temperature was determined by making the runs at 70°, 90°, and 95°C. at seven different H ion concentrations each. The period of heating was 8 hours. The stock was washed with acid as above described since the results were found to be more uniform by that procedure. The data are given in Table IV. Only the

total nitrogen recovered in the solution and the amino acid nitrogen of the solution were determined since these data defined with reasonable completeness the progress of the hydrolysis.

Fig. 6 shows the percentage of nitrogen recovered in solution plotted against the  $p_H$  of the final solution, for the four temperatures studied. The 80° curve is drawn in from Fig. 1. The general type of curve remains much the same throughout, but the depression at  $p_H$  5 to 5.5 becomes less exaggerated at the higher temperatures.

In Fig. 7 the amino acid nitrogen of the solution is plotted against the  $p_H$  for the several temperatures, the 80° curve being drawn in from Fig. 3.

TABLE IV  
INFLUENCE OF TEMPERATURE ON HYDROLYSIS

	$p_H$	70°	90°	95°
Total N recovered per cent.	1.1	55.0	84.1	87.6
	3.4	25.1	74.9	79.8
	4.6	12.6	62.4	74.3
	5.5	14.3	55.0	73.0
	6.9	15.2	57.5	77.6
	9.5	31.2	65.0	79.9
	12.1	44.5	78.8	86.3
Amino N in solution per cent.	1.1	11.3	25.3	33.5
	3.4	4.2	16.8	25.0
	4.6	2.5	17.4	25.1
	5.5	2.8	16.1	23.2
	6.9	2.7	15.4	24.9
	9.5	5.9	24.0	36.5
	12.1	16.8	47.6	58.6

#### INFLUENCE OF PERIOD OF HEATING

A series of runs was made at seven different H ion concentrations, tests being made for total nitrogen recovered in solution and amino nitrogen of the solution at intervals of 6, 12, 24, 72 and 168 hours. The temperature was in all cases 80°C. The data are tabulated in Table V. Fig. 8 shows the curves for the nitrogen recovered in solution plotted against the  $p_H$  of the final solutions for the several periods of heating. The curve for the 8 hour period is drawn in from Fig. 1. At 72 hours the curve is nearly straight but at 168 hours a de-

pression occurs on the alkaline side. This is due probably to the loss of an appreciable quantity of nitrogen as ammonia under those conditions.

In Fig. 9 the amino acid nitrogen of the solution is plotted

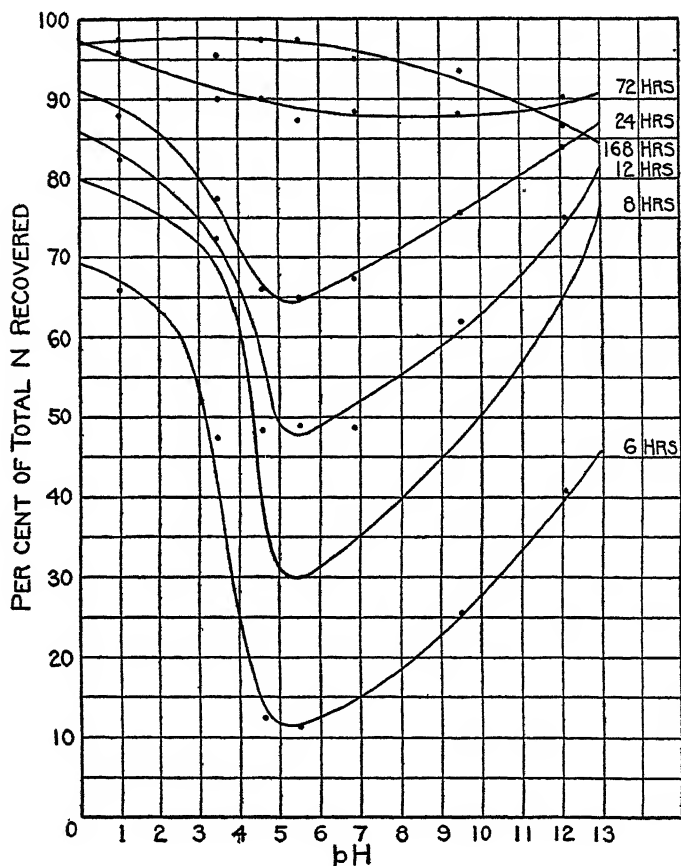


FIGURE 8  
EFFECT OF PERIOD OF HEATING ON TOTAL N RECOVERED  
IN THE SOLUTION AT VARYING pH

against the  $p_H$  for the several periods of heating, and the curve for the 8 hour period drawn in from Fig. 3. At 72 hours, from 70 to 80 per cent. of the nitrogen of the solution is amino acid nitrogen, and at 168 hours it reaches its maximum at

92 per cent. and drops on the alkaline side. This drop is also probably due to the formation of ammonia.

#### INFLUENCE OF RATIO OF STOCK TO WATER

Throughout most of the runs we used 500 grams of prepared stock and 800 grams of water. On the water-free basis this

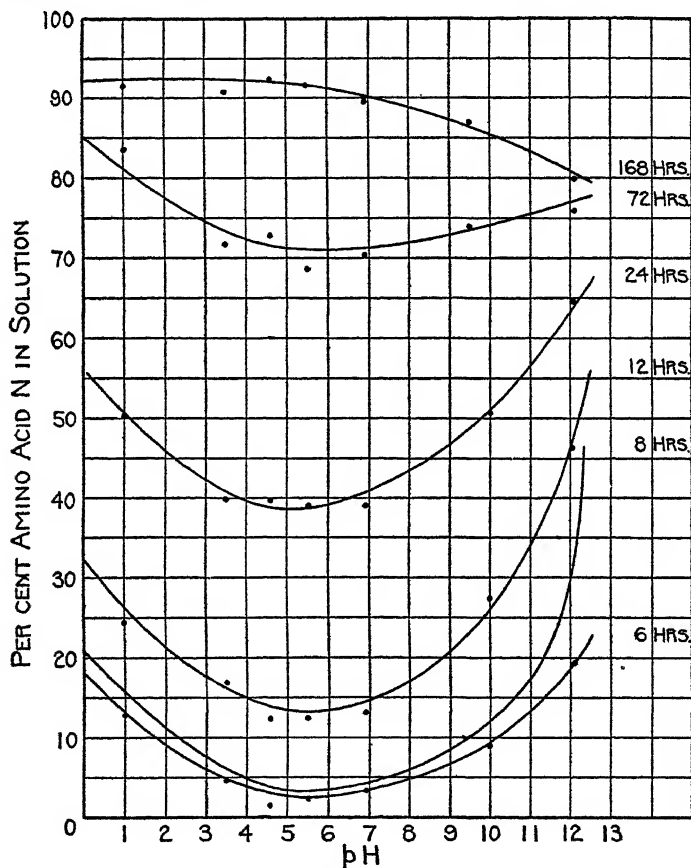


FIGURE 9  
EFFECT OF PERIOD OF HEATING ON AMINO N IN THE  
SOLUTION AT VARYING pH

became 98.85 grams of dry stock and 1201.15 grams of water, or practically 100 to 1200. This ratio was selected as the result of a few preliminary experiments. Ratios of 100 to

TABLE V  
INFLUENCE OF PERIOD OF HEATING ON HYDROLYSIS

	$\rho_H$	Period of heating in hours				
		6	12	24	72	168
Total N recovered per cent.	1.0	66.0	82.4	87.9	95.8	97.4
	3.4	47.4	72.5	77.6	90.0	95.5
	4.6	12.4	48.4	65.9	90.1	97.3
	5.5	11.5	49.0	65.1	87.6	97.5
	6.9	20.0	48.5	67.4	88.4	95.2
	9.5	25.7	62.0	75.6	88.2	93.5
	12.1	40.8	75.1	83.8	90.2	90.1
Amino N in solution	1.0	12.7	24.5	50.5	83.4	91.5
	3.4	4.8	17.0	39.9	71.6	90.8
	4.6	1.5	12.5	40.0	73.0	92.4
	5.5	2.4	12.5	39.1	68.8	91.9
	6.9	3.4	13.3	39.2	70.4	89.7
	9.5	9.0	27.6	50.8	74.0	87.0
	12.1	19.6	46.4	64.7	76.2	80.0

1400 and 100 to 1000 also were tried. The results of these preliminary runs indicated that increases in the water ratio hastened somewhat the hydrolysis of collagen to gelatin, and retarded slightly or was without influence on the secondary hydrolysis of the gelatin to its degradation products. A decrease in the water ratio showed the opposite tendency.

From these observations it would appear that a high water ratio was desirable as it would produce the greatest amount of undegraded gelatin, but in the gelatin plant the optimum amount of water to use would be limited by the necessity later

TABLE VI  
INFLUENCE OF RATIO OF STOCK TO WATER. (AVERAGE OF SEVERAL TESTS)

Dry stock, grams	Water, grams	Total N recovered in solution, per cent.	Amino N of solution, per cent.
100	1000	38.2	5.6
100	1200	41.8	5.1
100	1400	48.8	4.9

of evaporating off the excess, and in the present experiments it was desired to obtain a test for jelly consistency, and this would not have been feasible with the 100:1400 ratio. The 100:1200 ratio was very satisfactory from this point of view,

while the 100:1000 runs showed a smaller recovery of nitrogen in the solutions, and a slightly greater secondary hydrolysis. The 100:1200 ratio was, therefore, adopted for this investigation.

The data obtained are shown in Table VI.

#### EFFECT OF AGITATION

A few tests were made to determine the effect which agitation would produce on the hydrolysis. This was accomplished by blowing air through the hydrolyzing mixture. The air was first passed through potassium hydroxide and then through water at 80° and then into the stock solutions. Four different rates of flow were used, designated as rapid, medium, slow, and zero. The rapid was about ten bubbles per second; the medium about four; and the slow about one.

The results indicate that a rapid agitation hastens the primary hydrolysis of collagen to gelatin, but is without influence on the degradation of the gelatin. A rate of about two bubbles per second was employed throughout most of the experiments in this investigation. Table VII shows the results of these tests.

TABLE VII

EFFECT OF AGITATION ON HYDROLYSIS. (AVERAGE OF SEVERAL TESTS)

Rate of flow in bubbles per second	Total N recovered in solution, per cent.	Amino N of solution, per cent.
10	51.3	5.2
4	46.2	4.9
1	41.5	5.0
0	40.7	4.8

#### EFFECT OF CONDITION OF STOCK

A casual inspection of any lot of hide stock for manufacture into glue will show that it is of very non-uniform material. Some of the pieces will be very thick and firm, others thin and limp. There will be a heavy layer of porous fatty material on the flesh side of some pieces and none on others. Some pieces will be covered with hair and other pieces will be entirely free of hair. The moisture content of these several types will also vary greatly. It is obvious, therefore, that very careful selection must be made if results of fair uniformity are to be obtained.

The size to which the pieces are cut for the hydrolysis was found to influence greatly the rate of the reaction. Runs were made using large thick pieces; strips about two inches long by a half inch in width and thickness; and pieces cut to approximately quarter inch cubes. The recovery of nitrogen in the solution was much more rapid with the more finely cut pieces, and the secondary hydrolysis was also greater due to the longer exposure of the gelatin produced. This latter degradation could be averted largely, however, by employing a shorter period of heating. It would seem that this should be of importance in the manufacturing processes, for by cutting the stock into very small pieces the hydrolysis of collagen to gelatin is accelerated, a shorter period of heating is required, and there will then be less opportunity for the gelatin to become further degraded. A larger yield of higher grade product should result.

These data are given in Table VIII.

TABLE VIII

EFFECT OF SIZE OF STOCK PIECES ON HYDROLYSIS. (AVERAGE OF SEVERAL TESTS)

Size	Total N recovered in solution, per cent.	Amino N of solution, per cent.
Large irregular pieces	39.4	5.1
2 x 1/2 x 1/2	42.0	5.2
1/4 x 1/4 x 1/4	56.7	6.8

#### THE PLUMPING REAGENT

The rate with which the collagen passes into solution is dependent in large measure upon the treatment which it has received prior to the hydrolysis. As a result of a series of swelling experiments, five reagents were selected as of especial merit, and the hide pieces swollen in them were subjected to hydrolysis and several tests made on the resulting solutions. The results are tabulated in Table IX.

The water content of the dry salted stock before treatment of any kind was 34 per cent. After thoroughly washing, during which process the salt, dirt, hair, etc., was removed (amounting to 33 per cent. of the dry matter of the stock), the stock contained 70 per cent. of water. As will be seen from the above table the water content was raised from 70 to 89 per cent. in the lime solution, to 86 per cent. in the lactic acid solution, and



TABLE IX  
EFFECT OF PLUMPING REAGENT ON HYDROLYSIS

Reagent	Ca(OH) <sub>2</sub>		MgCO <sub>3</sub> + NaOH		Lactic acid		Borax		Boric acid	
Concentration	5%		5% + 0.2%		1%		5%		5%	
Stock:	89.0		78.1		86.0		80.0		77.5	
Water	14.09		14.21		14.13		14.00		14.08	
Total N										
Solution:										
Volume.....	1200	1200	1200	1250	1050	1050	1000	1000	1000	1000
N in solution.....	82.4	82.3	76.4	77.2	70.6	67.1	78.8	74.6	71.3	72.5
Amino N.....	5.4	5.4	8.2	8.3	3.8	3.6	5.1	4.8	3.9	4.0
N of residue.....	17.6	17.7	23.6	22.8	29.4	32.9	21.2	25.4	28.7	27.5
Viscosity.....	85	86	115	107	146	126	128	135	105	114
Jelly strength.....	liquid	liquid	25	21	22	18	25	29	20	24
pH.....	9.2	9.2	8.8	9.0	4.2	4.2	7.9	7.9	4.9	5.0

to lesser amounts in the others. But although the water content of the lime and lactic acid swollen stock was about the same, the physical condition was quite different. The former was firm and showed what might be called turgor. The latter was very limp and water could be easily squeezed out of it.

The lime soaked stock gave the highest yield of nitrogen in the solution, and a moderate amino acid content. The highest viscosity and swelling were obtained with the borax, and the lowest amino acid content with the lactic acid. These irregularities may be in part accountable to the fact that equal weights of the swollen stock were employed in the hydrolysis rather than weights which would be equivalent on the dry basis. In general, however, the alkaline swelling reagents yielded a product that was firm and went most easily into solution, but the excessive hydrolysis into amino acids was more pronounced than in the acid swollen stock. The latter was limp but gave solutions of good viscosity and jelly consistency.

#### GENERAL DISCUSSION

The experiments described in this report have shown that many conditions affect the hydrolysis of collagen to gelatin. Of these, the hydrogen ion concentration of the hydrolyzing solution, the temperature, and the duration of heating are apparently of greatest importance. All the curves recorded

have been plotted against  $p_H$ , and in all cases a minimum is observed in the region of the isoelectric point (between  $p_H$  4.5 and 5.5), and in every case, except the curve for ammonia evolved, the curves rise more or less rapidly on either the acid or alkaline side of that point. In the case of the ammonia evolved during the hydrolysis, the curve rises rapidly upon increasing concentrations of alkali, but remains uniformly low (practically negligible) at  $p_H$  values less than 5.0

The nitrogen recovered in the solution rises very rapidly on the acid side of the isoelectric point, increasing from about 30 per cent. at  $p_H$  5.0 to about 70 per cent. at  $p_H$  3.5. On the alkaline side the change is less rapid. The amino nitrogen of the solution remains low over a much greater range of  $p_H$ , but above 9.0  $p_H$  this form of hydrolysis increases very rapidly.

The viscosity and jelly strength curves are nearly parallel and show two maxima: one on the acid and the other on the alkaline side. The depressing effect due to the presence of salts (of calcium) in solution is shown especially well by these curves, for on the acid side much higher maxima are reached when the stock has previously been freed of these salts. The maxima come at about  $p_H$  3.5 and 8.0.

An increased temperature and a lengthened period of heating produce, throughout the entire range of  $p_H$ , an increased hydrolysis both of collagen to gelatin (as shown by the nitrogen recovered in the solution) and of gelatin to its degradation products (as shown by the amino nitrogen of the solution). At very long periods of hydrolysis, however, (168 hours) there appears on the alkaline side a drop in the nitrogen recovered in the solution. This is very probably due to the increased loss of nitrogen as ammonia under these conditions.

Theoretically, the most favorable results will be produced by a high ratio of water to stock, for the concentration being less, it is shown that more of the stock will go into solution during a given period, and this will be degraded to a lesser extent than if concentrated, but practically a limit is set to the optimum dilution by the necessity later of evaporating the water off again to produce a liquid that will gel when cooled.

Agitation is also shown to hasten the hydrolysis, probably by keeping the concentration of the solution that is in direct contact with the stock as low as possible by disseminating the

freshly dissolved material through the mass. The degradation to lower products is also increased slightly by agitation.

Very small pieces of stock were found to be dissolved with much greater rapidity than large pieces. The secondary hydrolysis was also increased, but it seems probable that a shorter period of heating or a lower temperature could advantageously be utilized with finely cut material.

Alkaline plumping or swelling reagents were found to yield a stock that was firmer than acid plumped stock, and that dissolved somewhat more rapidly, but a larger amount of the solution was degraded. Acid plumped stock was limp, but gave a product of good viscosity and jelly consistency.

There was no evidence obtained which would indicate that ammonia was evolved upon the hydrolysis only of collagen to gelatin. That ammonia was evolved upon the alkaline hydrolysis of collagen was demonstrated, but from the examination of the curves showing the amino nitrogen production upon the same treatment it appears that the ammonia nitrogen formation may be adequately accounted for as being due to a more complete breakdown of the molecule. Amino nitrogen can be increased only by hydrolytic scission of the large molecules. The formation of proteoses or peptones as well as of free amino acids, increases the amino nitrogen determinable. That this same operation produces also ammonia has been shown in the hydrolysis of gelatin by Fischer,<sup>9</sup> Dakin,<sup>10</sup> Van Slyke,<sup>11</sup> Bogue,<sup>12</sup> and others. It seems probable to the writer that collagen is a polymerized complex of gelatin. Upon heating gelatin to 130°C. an anhydrid probably is produced, but this is not similar to the original collagen. The polymerization seems to be chemical rather than physical, and would therefore be comparable to the relation between gelatin and proteose, or between proteose and peptone. Neither of the latter may be treated to reproduce gelatin, and it seems very doubtful if gelatin may be treated so as to reproduce collagen.

The optimum conditions for hydrolysis of collagen to gelatin are, of course, those by which the greatest amount of nitrogen passes into solution in the shortest period of time, but during

<sup>9</sup> Fischer, Levene and Anders, *Z. physiol. Chem.*, **35**, 70 (1902)

<sup>10</sup> H. D. Dakin, *J. Biol. Chem.*, **44**, 524 (1920)

<sup>11</sup> D. D. Van Slyke, *J. Biol. Chem.*, **10**, 43 (1911)

<sup>12</sup> R. H. Bogue, *Chem. Met. Eng.*, **23**, 156 (1920)

which process the minimum amount of degradation of the gelatin takes place. In the experiments reported, these conditions seem to be best attained by the following control:

The hydrogen ion concentration of the hydrolyzing solution should be such that the resulting gelatin or glue solution will possess an H ion concentration between  $p_H$  3.0 and 4.0 or between  $p_H$  7.5 and 8.5. The region of  $p_H$  4.5 to 6.0 should be avoided as the hydrolysis is very slow at that concentration of hydrogen ions. Above  $p_H$  8.5 the degradation of the gelatin becomes too great, with a corresponding loss of nitrogen as ammonia, and below  $p_H$  3.0 there is also a degradation, while in both cases the viscosity and jelly strength of the product becomes very low.

A temperature of 80°C. seems most favorable, and an 8-hour period of heating is satisfactory. There is too little hydrolysis at lower temperatures or shorter periods of heating, while at higher temperatures and longer periods the greatly increased degradation of the gelatin offsets any advantages of more rapid collagen hydrolysis.

The optimum ratio of dry stock to hydrolyzing solution (including water in the stock) seems to be about 1 to 12 or 1 to 14. Lower concentrations necessitate later evaporation, while greater concentrations give lower yields of gelatin and increased degradation of the gelatin formed.

The stock may be swollen in a number of different reagents, lime and lactic acid showing the best results to date, but the excess of reagent should be removed completely by washing and neutralization, as a depressing effect on the viscosity and jelly strength may result from their presence.

A fine cutting of the stock and constant agitation are desirable as they make possible a more rapid hydrolysis, but to prevent also a more rapid degradation of the gelatin a shorter period of heating or a lower temperature will be necessary. A 6 or 7 hour heating at a temperature of 75°C. probably will produce, with finely cut stock and thorough agitation, about the same hydrolysis as an 8-hour heating at 80° under the opposite conditions.

#### SUMMARY

Conditions affecting the hydrolysis of collagen to gelatin and of gelatin to its degradation products have been studied and

the results tabulated and discussed. The conditions studied include:

Hydrogen ion concentration	Ratio of stock to water
Presence of salts	Agitation
Temperature	Condition of stock
Duration of heating	The plumping reagent.

The evidence upon the constitution of collagen and its relation to gelatin has been discussed, and the findings of the present report brought to bear upon this problem, indicating that collagen is not a simple anhydrid of gelatin, but rather a polymerization complex produced by chemical condensation.

The writer wishes to express his indebtedness to Mr. C. K. M. Ritchie for performing a number of the determinations reported herein.

#### DISCUSSION ON R. H. BOGUE'S PAPER

#### CONDITIONS AFFECTING THE HYDROLYSIS OF COLLAGEN TO GELATIN

J. ALEXANDER: In appreciation of Dr. Bogue's valuable paper I would like to ask whether he has taken into consideration the time factor in the case of the reaction of these various things. If you carry the liming process a little further on you find that a great deal of it washes away and you have a very big loss of gelatin. The higher the degree of hydration the more nearly does the collagen approach the gelatin itself. If my recollection is correct, I think Prof. Thomas made some experiments recently to show that the behavior of the digestive portion depends very much upon the state of swelling of the collagen. The same is true with other proteins.

R. H. BOGUE: In reply to Mr. Alexander, in my preliminary experiments I studied the optimum for each reagent and so when I came to this special set I made use only of that optimum time.

J. A. WILSON: I might point out a very interesting fact,—if you treat hide with trypsin you get immediate action, but if you apply that same thing to uncured skin the trypsin is apparently without action for about twenty-four hours. It is just a curious time factor that is involved, I suppose.

J. ALEXANDER: Wouldn't there be a swelling factor?

J. A. WILSON: Apparently not.

J. ALEXANDER: There seems to be something that causes that delay in solution.

J. A. WILSON: But the same thing happens with a perfectly fresh skin as one that has been in lime.

J. ALEXANDER: Still there seems to be something that is responsible for that delay.

J. A. WILSON: There may be.

D. KLEIN: That observation of Mr. Wilson does not quite apply to ordinary skin on one's hand. If you take an ordinary solution of trypsin and get it on your fingers, within two or three hours you will notice around the nails that your skin is eaten away and your fingers begin to bleed.

J. A. WILSON: Fresh calf skin taken off from an animal within an hour of its killing, placed in a trypsin solution has no effect epidermally in twenty-four hours, and when action does begin it begins from the flesh side and eats through.

D. KLEIN: Do you know whether that skin has been treated at all in any way?

J. A. WILSON: I am referring to a skin taken right off the animal's back within an hour after its death.

J. ALEXANDER: During life the hydrogen ion concentration in a living organism is somewhere around  $p_H$  4.5 and after death it changes over to  $p_H$  6.5. Now, there is a time factor involved there.

H. C. BRADLEY: That happens very rapidly. It is a matter of minutes.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, WILSON  
AND CO., CHICAGO]

## THE COLLOID CHEMICAL PROBLEMS IN THE MANUFACTURE OF ENZYMIC AND ANIMAL GLANDULAR PRODUCTS

BY DAVID KLEIN

My purpose in presenting a paper on this subject is not so much that it be a record of achievement, but rather that it serve to give some idea of what there is for a colloid chemist to do in the commercial sphere. As the problems are unfolded, it will be recognized that they are not entirely peculiar to this field, but are met with in every industry having to do with matter that once was living. The basic material is of animal origin. It consists, among others, of proteins and related substances, of lipoids, fats, cholesterin, salts, coloring matters. These affect the properties of the others profoundly; solubilities of the pure or isolated substances no longer apply. In many cases the solubilities, precipitations, coagulations, are even influenced by the order in which the ingredients are put together.

The finer mechanism of living tissue, that regulates the permeability, the selective manifestations of the live cell is of course gone, but imbibition and swelling are still to be reckoned with, in such processes as extraction, washing, filtering and handling in general. These manufacturing steps are of extreme importance from a production standpoint, since the cost of a product may be seriously affected by undue labor costs. There is the further consideration, that is paramount in offering a product for sale, *viz.*, uniformity. Unfortunately, the basic material is not uniform, and many of the problems resolve themselves into ways of modifying factory processes so that the finished product shall not show this variation.

The foregoing generalities may take on added significance if direct application is made of them, to certain of the products as offered commercially. Roughly, the substances that will be discussed may be classified under the three headings:

1. Enzymes
2. Gland products
3. Catgut

The animal enzymes that are commonly used are pepsin, rennin, and pancreatin (trypsin, diastase, lipase). Pepsin is derived from the mucous lining of the stomach of the hog (or other animals), by digesting it in water containing hydrochloric acid at a temperature of 110–120°F. If the digestion is properly carried out at the end of four to six hours practically all of the linings will have been dissolved, yielding a yellowish, turbid fluid, which can be clarified by suitable filtration means. The liquid can then be concentrated *in vacuo* and dried at a low temperature. However, such a pepsin is a very crude article and is not likely to be satisfactory because it produces turbid elixirs that are clarified only after much labor and trouble. Further, such a pepsin contains peptones that are exceedingly hygroscopic and may result in the pepsin becoming sticky or pasty during transit or storage.

Pepsin diffuses much more slowly through parchment than do peptones, salts and acid. So it is possible to make pepsin of higher digestive power, containing less peptone and acid, by dialyzing with parchment paper. The method is inefficient, costly and antiquated. Anyone who has attempted dialysis on a commercial scale will appreciate the technical difficulties of the process, and the reasons for seeking a better way of preparing pepsin.

Advantage is sometimes taken of the salting out action of sodium sulphate. This yields a pepsin of high strength (1-10,000) with the additional advantage of being non-hygroscopic. Such a pepsin is excellently adapted to tablet use, but is not suitable for solutions.

It is possible to purify pepsin by the use of organic solvents. Alcohol, acetone, or other dehydrating solvents can be used. I have here a very crude pepsin concentrate. By the addition of alcohol, there is formed a large, gummy precipitate. Removing this, and adding more alcohol causes a further precipitation, rich in pepsin. Most of the peptones, coloring matter, and salts remain in solution. The yield and strength of pepsin produced by this method are governed by many factors such as concentration of original pepsin solution, temperature,  $p_H$  value and concentration of solvents.

Rennin is an enzyme that is extensively used in cheese-making. It is derived from the stomach of the calf and is offered



commercially in two forms, liquid or solid. Rennin deteriorates rather rapidly, especially in solution. In this connection, it is interesting to note that peptones exert a very pronounced protective action, whereby the stability is increased. Here again such factors as concentration,  $p_H$  value, and apparently the order in which the ingredients are added, influence the keeping quality of the liquid rennet prepared by this method.

Rennin is soluble in dilute sodium chloride solution, but is precipitated by saturating with salt. In this way, it is possible to prepare a very high testing product. From a commercial standpoint it is desirable that the precipitate be compact and readily handled; otherwise much labor is expended, and a poor yield obtained. Among the factors which control the character of the precipitate are concentration,  $p_H$  value and temperature.

The diastatic enzyme of the pancreas is extremely labile. Even in dry form, in a well stoppered bottle, it loses its activity more rapidly than is desirable from a commercial standpoint. Despite the large amount of work that has been expended on this enzyme, more study should be devoted to problems of rendering diastase more stable.

Turning now to the animal glandular derivatives, the problems encountered are somewhat different and more difficult. Where extracts of the glands in ampoule form are offered to the physician for hypodermatic use, the following characteristics are of extreme importance:

1. Stability of potency (the longer, the better)
2. Brilliancy of appearance, which must be permanent
3. Non-toxicity
4. Sterility
5. As water clear as possible
6. Uniformity

As an illustration of the colloid-chemical problems involved in the preparation of such extracts, let us consider pituitary extract. This is derived from the posterior lobe of the pituitary body, and has the remarkable property of causing involuntary muscle to contract. For this reason extensive use is made of it in obstetrics and after operations. Despite the numerous investigations that have been made upon the chemical identity of this active principle of pituitary extract, very little headway has been made towards its chemical identifica-

tion. This much is known; that it must be extracted and maintained in an acid medium. The stability of the potent substance is dependent upon the  $p_H$  value. If it is more than 5.0 there is a big loss of activity even during the extracting from the glands. If the  $p_H$  is low, say around 2.5, there is deterioration after a few months. Most commercial extracts have  $p_H$  values between 4.2 and 3.8.

The clarity of the solution and the rapidity of filtration are also functions of the  $p_H$ . A solution which is very clear and bright when made, may cloud up after twenty-four hours, and be unfit for sale unless reclarified. It sometimes happens that an extract will show no precipitation when boiled, yet the sealed ampoules of the same lot when sterilized below the boiling point will show a precipitation that renders them unsalable, although the potency will not have been reduced. I should like to emphasize at this point, the variations that exist in successive lots of glands, despite their soundness and similarity of methods of handling. This is true not only of the pituitary, but also of all the other glands. It is this variation, that makes necessary a knowledge of colloid chemistry.

Recently other gland extracts have been put on the market, such as corpus luteum, ovarian substance and parathyroid. Very little is known of the chemistry of these glands, or of methods for the identification of their active principles. In fact one of the outstanding problems in the field of organotherapy is the devising of methods of identification and assay, to say nothing of the actual isolation, of the active substances. The lipoids of the various glands have not been studied enough, probably owing to the difficulties attending their isolation, such as ease of oxidation, with concomitant changes in solubilities and precipitation reactions.

Another subject of extreme colloid-chemical interest is surgical catgut. Despite its name, this product is derived from the intestine of sheep. Briefly, the process of preparing catgut is this: Washing the gut, splitting into so-called rough side and smooth side, removing fat and other substances through sliming machines, bleaching, twisting, drying and polishing. The finished strand should be smooth, soft, pliable, uniform in gauge, elastic and of good tensile strength. Of these, softness, pliability, elasticity and tensile strength are dependent upon

the preservation of the cell structure of the original intestine. Any change in the composition of the cell wall, in the swelling properties of the cells will be reflected in one or all of the above desirable qualities of the finished gut. There is a natural lack of uniformity of size and strength in the raw intestine; add to this deterioration through bacterial or enzymic agencies and you will appreciate the difficulties of the problems.

The raw catgut is not suitable for surgical purposes, owing to its great bacterial contamination, part of which are spore formers. The gut must be sterilized, and is usually offered to the surgeon in sealed tubes, in one of two varieties, boilable or non-boilable. The former term signifies that the tube may be immersed in boiling water, to sterilize the outside (the contents are sterilized by the manufacturer). A non-boilable catgut cannot be boiled, but must be sterilized cold. The tendency of the medical profession is for boilable catgut.

In order to prepare a boilable catgut, all water must be removed, otherwise the catgut will "cook up" when the tube is placed in boiling water. The way the strand is dehydrated is highly important, since it is easy to convert the cell protein into gelatin, with a resultant loss of tensile strength.

After dehydration, the strand is covered with a suitable anhydrous tubing fluid, the tube sealed and sterilized at a temperature which will render the strand sterile. The conditions are essentially those of dry heat sterilization and the temperature required is obviously high, around 150°C. for a half hour or longer. From a chemical standpoint, the sterilization process is also one of destructive distillation. There is a partial decomposition of the strand, with a consequent loss of tensile strength.

From the foregoing, it will be readily seen why a finished tube of boilable catgut does not possess the flexibility, elasticity or tensile strength of the raw strand. Dehydration removes the important factor, water, that endows the raw material with its desirable properties. Heat fixes the cells and alters the composition of the cell wall and contents, so that, even when water is added, the catgut is never quite the same as it was originally. The ideal catgut, of boilable grade, with the softness, and elasticity of a non-boilable, has not been wholly achieved. Its attainment is distinctly a colloid-chemical

problem. The pliability is not due to the  $\text{OH}^*$  of the water since a substance such as glycerine instead of endowing catgut with pliability, actually makes it brittle due to the dehydrating properties of the glycerine.

Catgut is a very hygroscopic substance. Use of this property is made in the construction of hair hygrometers. If a looped strand of catgut is placed in a tube, and then dried out in a water oven, it will be found that the coil has assumed more or less a figure eight, which we call a dry twist. If an anhydrous fluid such as toluene is placed on this gut, the tube sealed and heated to  $290^\circ\text{F}$ . in an oil bath, it will be found that the strand has returned to the straight condition. If the tube be heated to a higher temperature, say  $325^\circ\text{F}$ ., or if the gut were not sufficiently dry to begin with, it will be observed that the gut has assumed a figure eight form, which we designate as a wet twist. There is no difficulty in distinguishing wet twists from dry ones since the looping is in opposite directions, a dry twist having this direction  $\text{S}$ , while a wet twist has this one  $\text{Z}$ . The changes in shape of the looped strand are satisfactorily explained on the basis of the moisture content and its relation to the hydration of the cells.

The foregoing should serve to illustrate the types of colloid chemical problems of the animal gland industry. I think you will agree with me that there is ample opportunity for research of the highest type.

#### DISCUSSION ON D. KLEIN'S PAPER

### THE COLLOID CHEMICAL PROBLEMS IN THE MANUFACTURE OF ENZYMIC AND ANIMAL GLANDULAR PRODUCTS

J. A. WILSON: This demonstration is very illuminating to say the least, and it gives us some idea of the complexity of some of the problems that we meet with in the industries. I am sure that you are all anxious to give Dr. Klein a ready hand in the solution of his numerous problems.

J. H. MATHEWS: You say sometimes the material (pepsin) clings together, while other times it does not. Suppose you took some of this stuff that would cling together and "slush" it around, will that cause it to coagulate?

D. KLEIN: No; instead of the material coagulating it forms one mass of blubber, I call it, with no liquid oozing out of it at all.

J. H. MATHEWS: I was wondering whether it was a matter of resistance to coagulation; that was what I was really getting at.

D. KLEIN: We can't coagulate it.

J. ALEXANDER: Have you tried to get the gold numbers to see whether they vary?

D. KLEIN: No.

J. ALEXANDER: It is barely possible that it might throw some light on the difficulties you have. It occurs to me that you might have here an existence of a cumulative colloidal protection. It is generally known of course that gelatin is a very good protector. If you have a certain substance which I will represent here by A, and another by B, there is no reason why B cannot be affected by C, and so on. It is just like a house of cards, if any one of the links or cards is weak or disturbed the whole thing may collapse. The whole thing seems to hinge, as far as I can see, upon that, or I imagine it might all depend upon the protein action varying so that in some cases although you may not have a difference that is very large in itself, you still may have a wide difference in the end.

I am very certain that everybody very greatly appreciates the very interesting subjects you have given us for thought and the possibilities it gives us for research work. We are also very interested to see that things are seldom what they seem.

H. N. HOLMES: I would like to ask whether you said that fuller's earth would take up these enzymes?

D. KLEIN: I did not say it, but they do. You can adsorb a large number of these enzymes under certain conditions.

H. N. HOLMES: How would you get it out of the earth, then?

D. KLEIN: By water, acidified or made alkaline as required.

H. N. HOLMES: The reason I asked the question was that I thought something of that sort was true. It seems to me that the silica gel might be of possible use in that connection.

D. KLEIN: Is it alkaline?

H. N. HOLMES: No; it is made with an excess of acid and

then thoroughly washed. And in that connection I was wondering whether you could force out or increase the adsorption on that or any other material, if to the watery extract you added insufficient alcohol to coagulate it but enough to bring it to nearly the coagulating point. It would seem to me that each one would help the other, then, and that you might carry it over.

D. KLEIN: Then the problem comes, in how many thousand gallons would you have to operate in order to make a hundred pounds of pepsin. It takes a lot of washing in order to get the stuff removed.

E. F. BURTON: Have you ever tried using a centrifuge?

D. KLEIN: No. That colloidal fluid will stand for months that way.

J. ALEXANDER: What does the ultramicroscope show?

D. KLEIN: I don't know; I have never tried it.

J. A. WILSON: Regarding the effect of acid on the rate of filtration, that of course is true in a great many substances. We thought the material when you tried to centrifuge it would throw out some of the material and cause some of the rest of it to be more dispersed.

D. KLEIN: That is very true.

R. H. BOGUE: Mr. Klein spoke about the variation in that stuff there (indicating) with time. I would like to ask if it varies in a regular way and just what the nature of that variation is.

D. KLEIN: I can't tell you, because so far we have not been able to determine if it was a regular variation or an irregular variation. We know the material becomes thicker on standing, and that it is more difficult to coagulate, and we have to use different concentrations the longer we let it stand, and this (indicating) has occurred at ice-box temperature of from 38 to 40°F., where after two months the material was entirely different from the material we put in there. Now just what the change is we haven't determined.

R. H. BOGUE: In regard to the gluiness of that mass that has precipitated, is that water soluble?

D. KLEIN: Yes; it goes into solution rather well.

R. H. BOGUE: Does it produce a jelly?

D. KLEIN: No. Ordinarily it will not gel.

R. H. BOGUE: Let us suppose this situation (drawing diagram on board). Now if the membrane that surrounds the cells is a colloidal membrane, I would like to ask some explanation as to how the enzyme manages to get through.

J. A. WILSON: I wonder if they do go through. You will find that the enzyme will not penetrate under all conditions. In the collagen portion you are not dealing with cells but with material that is produced by these migratory cells, and that is attacked very readily. It will not pass through an epidermal layer.

J. ALEXANDER: With reference to the question that was asked some time before, a good many people seem to think that when a substance is colloidal it does not diffuse. Graham simply said, or mentioned the fact that colloids diffuse slower than crystalloids. Those things do diffuse, but they haven't the speed of the others. The great trouble lies in the fact that many textbooks have a lot of things in them that are positively erroneous.

# THE COLLOIDAL STATE IN METALS AND ALLOYS

BY JEROME ALEXANDER

Few natural phenomena are as simple as are the scientific theories advanced to explain them. In nature a multiplicity of forces, laws, and tendencies are operative, whereas the framers of theories, aiming at simplicity, omit from their calculations many factors which at the time are unknown, obscure, or regarded as negligible or unimportant.<sup>1</sup>

Formulae and even "facts" which fit in with our observations under a given set of conditions, may fail if conditions change or if the keenness of our observation is increased. Every building is built on the assumption that all plumb lines are parallel, although we know that those at Madison and those at Rome are about at right angles to each other. Van't Hoff introduced the rather important factors  $a$  and  $b$  into the equation expressing the relation between volume, temperature and pressure in gases, and recently Einstein showed that the "Laws" of the immortal Newton are only approximations but so close to the actual truth, that it requires the most minute observation of an  $\alpha$  particle moving with a velocity upwards of 10,000 miles a second, of the precession of the orbit of the most rapidly moving planet Mercury over a lapse of centuries, or of a slight deviation of a light ray at the time of a solar eclipse, to give discernible variations from their apparently universal sway.

## EFFECTS OF IMPURITIES

If we could but choose our experimental conditions so as to rule out all disturbing and Bolshevik factors, Science might be simplified; but it would not then accord with Nature, which, as Poincaré succinctly remarked, is not as simple as all that. In dealing with metals we find that it is exceedingly difficult if not impossible to secure pure products, and with alloys the same difficulty exists and is compounded. Unknown "impuri-

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<sup>1</sup> Dalton's theory, which underlies the whole of modern chemistry, is based on the assumption that all the atoms of any one element are alike, an assumption now proved to be erroneous by the researches of Aston, Harkins and others. Thus there are three different kinds of chlorine atoms, with atomic weights of 35, 37 and 39, respectively, six different isotopes of mercury, and consequently 63 possible kinds of calomel. Here is a typical instance of a case where a theory based on a false postulate of equality of atoms arrives at a substantially correct result, because in nature the plus and minus errors balance each other



ties," dissolved gases, and the like, produce effects which we are beginning to appreciate and take notice of seriously.<sup>2</sup> Really pure iron is a rare metal.

Small traces are not to be sneered at nowadays, especially since the surprising results reported by Prof. H. B. Baker<sup>3</sup> who, on removing the traces of moisture existing in ordinary "pure" specimens of a number of elements and compounds by allowing them to stand some years over phosphorus pentoxide, found the following almost incredible changes in their boiling points:

	Years standing	Increase in boiling point
Bromine.....	8	55°
Mercury.....	9	62
Hexane.....	8½	14
Benzol.....	8½	26
Carbon disulphide.....	1	30
Carbon tetrachloride.....	9	34
Ethyl ether.....	9	48
Ethyl alcohol.....	9	60
Methyl alcohol.....	9	54
Propyl alcohol.....	9	39

These figures make us suspect that many of the constants tabulated with respect to various materials, may not apply at all to the strictly pure substances, and serve to give an inkling as to a possible cause for disparities in the results reported by different observers. Peculiarities of this general type are well known to physicians and biologists—thus Francis Carter Wood reports that certain selected strains of white mice are susceptible to the development of cancer, whereas others treated and fed under exactly the same conditions, cannot be made to develop it.

#### THE TIME FACTOR

Another fact of general importance in nature, having especial application to the phenomena met with in metals and alloys, is that many transformations occur so rapidly as to elude our observation, and compel us to draw upon our imagination to follow what happens between the initial point and the end-

<sup>2</sup> Thus U. S. Patent 1,432,607 granted to F. Milliken, Oct. 17th, 1922 specifies Cu, 80-70%, Ni, 9-12%, Zn 19-24%, Fe 1-2¼%, Mn a trace

<sup>3</sup> *Trans. Chem. Soc.*, **121**, 568 (1922)

point.<sup>4</sup> By photographs taken thousandths of a second apart, Rayleigh showed the curious differences that occur when various liquids are dropped into water.

In their article on "Alloys"<sup>5</sup> Roberts-Austen and Neville, in speaking of the copper-tin alloys containing less than 9 per cent. by weight of tin, say that upon quickly chilling small ingots from successively lower temperatures beginning just above the melting point, we thus learn that these alloys (bronzes) "although chemically uniform when solid, are not so when they begin to solidify, but that the liquid deposits crystals richer in copper than itself, and therefore that the residual liquid becomes richer in tin. Consequently, as the final solid is uniform, the crystals formed at first must change in composition at a later stage. We learn also that solid solutions which exist at high temperatures often break up into two materials as they cool...." The work of Beilby on plastic flow and of Benedicks on quick chilling, give an insight into the behavior of metals when stressed, worked and hardened.

What we lack mostly to-day is the ability to take a birds-eye view of science as a whole, and to correlate knowledge in diverse fields. To use a good old-fashioned term, we need natural philosophers, scientists who, while possessing extensive knowledge in one or more special fields, have nevertheless a sufficiently broad grasp of the general facts and principles of physics, chemistry, biology, geology, mineralogy and kindred natural sciences, to appraise and correlate correctly their own observations and the observations of others. The metallurgist and metallographer, secure in a highly developed technique of their own, dare not invade the sacred field of the inorganic chemist, and the inorganic chemist returns the compliment. The same applies to other branches. Unfortunately the feeling has arisen that there is something mysterious about metals, which only the closely initiated can comprehend. Even if this were true, the awed novice coming from another realm of science, might bring with him memories or might see relationships which the older votaries fail to notice.

<sup>4</sup> T. W. Richards [*Am. Chem. J.*, 26, 61 (1901)] followed microscopically by instantaneous photography, the separation of crystals from solutions, and reported that the initial growth is much more rapid than subsequent growth

<sup>5</sup> *Encyclopedia Britannica*, 11 ed. Vol. 1, p. 706

COLLOID PHENOMENA IN METALS<sup>6</sup>

Metals in their behavior exhibit many of the colloid chemical principles observed in other substances, and some of these will be considered. Among them are:

1. The colloidal state as affecting crystallization and grain size (including the effect of impurities).
2. Colloidal protection, including autoprotection (isocolloidism, and allocolloidism) and cumulative protection.
3. The zone of maximum degree of colloidality.

It may be stated as a general truth that no substance passes from true molecular dispersion to microscopically visible aggregation without passing through the colloidal zone wherein its particles or some of them are roughly from 5  $\mu\mu$  to 100  $\mu\mu$  in diameter. Thus high pressure steam on issuing from a pipe is colorless until by condensation it enters the colloidal zone, when it becomes visible as the familiar white cloud popularly termed "steam." These colloidal droplets may either aggregate to form a rain or else evaporate as they float. In either case, as they pass out of the colloidal zone, they once more become invisible.

There is a steady accumulation of evidence that the colloidal state exists widely and persists frequently. For instance R. W. Moore,<sup>7</sup> in growing large crystals of Rochelle salt, found that the crystals grew faster at the bottom of the crystallizing vessel than at the top, indicating a gravitational accumulation of crystallogen, or nuclei. Van Calcar and Lobry de Bruyn<sup>8</sup> crystallized about  $\frac{3}{8}$  of the sodium sulphate from a saturated solution of this salt at the periphery of a rapidly revolving centrifuge. Since this cannot be done with dilute solutions, the existence of relatively large and numerous molecular aggregates seems probable in concentrated solutions. Alexander and Bullowa<sup>9</sup> observed ultramicros streaming from a crystal

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<sup>6</sup> Many analogies between colloid phenomena and those observed in metals have long been recognized by some. Thus in an Inaugural Dissertation presented by Dr. H. Kneebone Tompkins to the University of London in 1896, but first published in 1920, as an appendix to the Report of the General Discussion on the Physics and Chemistry of "Colloids and Their Bearing on Industrial Questions," the author (pp. 185-186) points out many analogies between vulcanized caoutchouc and metals. Possibly earlier references can be found

<sup>7</sup> *J. Am. Chem. Soc.*, **41**, 1010 (1919)

<sup>8</sup> *Rec. trav. chim.*, **23**, 218-223 (1904)

<sup>9</sup> *Arch. Pediatrics*, **27**, 18 (1910)

of sodium citrate that was going into solution. W. E. S. Turner in his monograph on "Molecular Association" concludes his chapter on the selection and use of molecular formulae as follows: "the formula of a substance shall be recognized as a function of the physical condition under which it exists, so that the formula for elements is  $X_n$ , for compounds  $(XY)_n$ , where  $n$  is to be specified according to conditions. Although we are far from realizing how  $n$  varies for most substances, the adoption of such formulae will bring home clearly the fact that both the physical and the chemical behavior of a substance may be closely dependent on the value of  $n$ ."

According to Langmuir, ice consists of double molecules of water,  $H_4O_2$ , and much evidence is quoted by Turner<sup>10</sup> to show that water is associated, only steam containing mainly  $H_2O$ , whereas liquid water contains more complex molecules or molecular aggregates. In some cases, *e. g.*, with sulphur and phosphorus, there may exist a condition of dynamic equilibrium between allotropes.

#### BEHAVIOR OF SULPHUR

The work of Alexander Smith, and others has shown that when first melted, sulphur is a mixture of yellow mobile liquid,  $S_\lambda$ , with a relatively smaller amount of a brown viscous liquid  $S_\mu$ , the latter increasing in amount until it reaches 40 per cent. at the boiling point,  $445^\circ$ .  $S_\lambda$  is supposed to represent  $S_8$ , and  $S_\mu$  to represent  $S_6$ . There is a time lag in the formation of  $S_\mu$  with increasing temperature, and it is of great interest to note that ammonia, which in general serves as a deflocculator to colloids, catalyzes the transformation, while  $SO_2$ , which generally acts as coagulant, retards it.

Sudden chilling of the molten sulphur maintains the status quo, and by taking advantage of the fact that  $S_\lambda$  is soluble in  $CS_2$  whereas  $S_\mu$  is insoluble, a separation of the two allotropes may be made and their percentages estimated. By pouring a thin stream of sulphur heated to  $400^\circ$  into liquid air, von Weimarn<sup>11</sup> obtained a transparent, highly elastic sulphur. Here the rapid molecular aggregation and increase in viscosity consequent upon the drastic chilling were sufficient to inhibit

<sup>10</sup> *Loc. cit.*, Chap. 8

<sup>11</sup> *Kolloid-Z.*, **6**, 250 (1910)

the allotropic molecular rearrangement and also the further growth of colloidal particles, so that there resulted a dispersion of sulphur aggregates in still more finely dispersed sulphur—a sulphur sulphogel or solid sulphosol. Thomas Iredale<sup>12</sup> produced a similar elastic sulphur by mixing (in a draft closet) 150 grams of finely powdered sodium thiosulphate with 70 grams of concentrated nitric acid. The flexible sulphur undergoes a slow syneresis; the arrested molecular tendencies gradually establish themselves, and the mass becomes brittle and crystalline.

#### MOLECULAR AGGREGATION

In his article on "Isomerism"<sup>13</sup> J. H. van't Hoff points out the importance of polymorphism, which Otto Lehmann showed to be an almost general property, many substances showing a great variety of forms—ammonium nitrate shows at least four before melting. Conditions may be such that a less stable form may persist. Thus though polymorphous calcite is the more stable form of calcium carbonate, aragonite is of common occurrence and has existed through geological periods.<sup>14</sup>

When we consider solid metals, then, we must expect to find molecular aggregation to be rather the rule than the exception, and further that aggregations of colloidal dimensions are also to be expected in most cases, since when metals are cold the viscosity or rigidity is usually great enough to inhibit further molecular change within measurable time. However, such soft metals as lithium, lead, tin, etc, "temper" at room temperature.

#### A GENERAL PRINCIPLE UNDERLYING COLLOID PHENOMENA

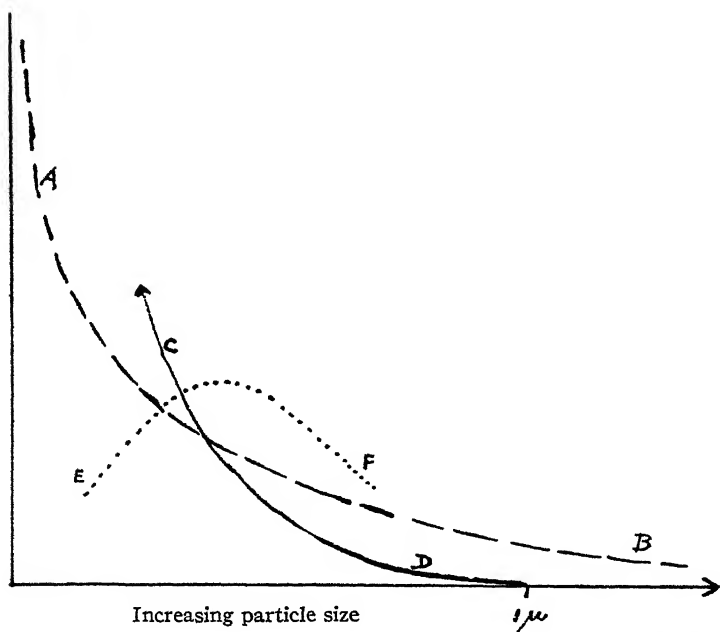
Now what is there peculiar to the colloidal state? Matter in the colloidal state of subdivision or dispersion has properties that are unique, anomalous, different from those of the same substance in the finer crystalloidal dispersion or the coarser macroscopic aggregation. What is the underlying basis of these peculiarities?

<sup>12</sup> *Kolloid-Z.*, **28**, 126 (1921)

<sup>13</sup> *Encyclopædia Britannica*, 11th ed., Vol. XIV, p. 884

<sup>14</sup> Contrary to W. Ostwald's classification, there appears to be a continuous transition between the so-called metastable and labile states. See de Coppet, *Ann. chim. phys.*, (8) **10**, 457; S. W. Young, *J. Am. Chem. Soc.*, **33**, 148 (1910)

The ultramicroscope shows that as substances begin to enter the colloidal zone of dispersion, the slight Brownian motion exhibited by particles near the limit of ordinary microscopic resolvability (about  $\frac{1}{4}\mu$ ), increases rapidly, so that particles about  $50\mu\mu$  have a very active free path motion. We have as yet no data which will enable us to plot the curve showing the



AB = free surface per gram; CD = kinetic motion curve; EF = rise and fall of colloidal characteristics.

Fig. 1.—Relation between kinetic activity and specific surface.

rate of increase in kinetic motion. Particles about  $1\mu$  in diameter are practically motionless while those about  $5\mu\mu$  move many feet per second; so that the curve must rise sharply.<sup>15</sup>

The free surface per gram, however, already very great with particles  $1\mu$  in diameter, increases as the square of the diameter and must plot as an hyperbola, which approaches and crosses

<sup>15</sup> J. Alexander, *Science*, **46**, 663 (1922).

the kinetic motion curve. See Fig. 1. Colloidal particles have therefore a kinetic motion disproportionately large when compared with larger particles, and disproportionately small when compared with smaller particles. Some of the consequences of this will be considered later when discussing the zone of maximum degree of colloidity.<sup>16</sup>

Of course in the colloid state the free surface is enormous. Consequently "surface forces," probably due to unsatisfied electronic fields, are enormous, and register their influence in surface tension, adsorption, etc. The tiny force with which a rain drop clings to the window pane becomes important when the surface is magnified millions of times.<sup>17</sup>

#### PURE METALS

Let us now consider the case of pure metals. The general rule is that when quenched, they are harder than when slowly cooled; as is evidenced by the following results: (Experiments of W. A. Cowan reported by J. Alexander.)<sup>18</sup>

	Brinell number
Straits Tin—chill cast.....	8 8
“ “ slowly cooled.....	7 7
Corroding Lead—chill cast....	5 2
“ “ slowly cooled..	4.4

These metals were quite pure, although in the results the effect of impurities is undoubtedly registered. The tendency of quick chilling is to keep the crystals of metal small, increasing the intercrystalline surface.

<sup>16</sup> Another point of view is that the effects of gravitation vary as the volume, that is the cube of the diameter, whereas the surface forces vary as the square of the diameter. An interesting illustration of the anomaly of the colloidal state is found in the tails of comets. (See J. Alexander, "Colloid Chemistry," D. Van Nostrand Co., 1922; *Oil, Paint and Drug Reporter*, 1923.) Usually, their particles are of colloidal dimensions, and are repelled from the sun, because as J. Clerk Maxwell has shown, in the case of colloidal particles, the light-pressure overcomes the attraction due to the sun's gravitation. Baade's comet, at present visible, shows in addition, a phenomenon of somewhat rarer occurrence—that is, some tails pointing toward the sun. It seems possible that these heliocentric tails are composed of particles at or above the upper range of colloidal dispersion, so that with them the sun's gravitational attraction exceeds light repulsion.

<sup>17</sup> W. O. Fenn (*J. Gen. Physiol.*, 5, 311 (1923)) reports that very small particles of quartz or of carbon (less than  $1\mu$  in diameter) are less readily ingested by leucocytes than are larger particles of the same material, though this is contrary to what surface tension would lead one to expect.

<sup>18</sup> *J. Trans. Am. Inst. Min. and Metal Eng.*, 1920; *Chem. Met. Eng.*, Vol. 26 (1922)

A similar effect is produced by cold working.<sup>19</sup> Thus Zay Jeffries reports<sup>20</sup>

	Brinell hardness numbers
Cast tin, large grain.....	9.12
Cold-hammered tin.....	11.32
Cast lead, large grain....	5.44
Cold-hammered lead.....	6.54

The cause of this increased hardness is increased fineness of grain, resulting in greater free surface and surface forces. Furthermore because of the variation in the direction of the axes of the small crystals, there cannot be any considerable sliding of metal along any one long line of crystal cleavage where the metal is weakest. To account for planes of relatively easy cleavage, we may imagine that the metal atoms, when arranged in their regular crystal lattice, are so placed that the most powerful plus and minus poles or zones are opposed, leaving the weaker zones to unite with a weaker bond. Large regularly formed crystals would therefore be weaker along these large areas of inferior attraction, whereas small crystals have their planes differently oriented.

### ALLOYS

When we consider the behavior of mixtures of metals, we find a series of phenomena which are of general, widespread occurrence.<sup>21</sup>

In the first place when metals are fused together, there usually results an extremely intimate mixture known as an

<sup>19</sup> J. A. Mathews (*Bull. Am. Inst. Mining and Met. Eng.*, No. 149, p. 788, May, 1919) reports the following Izod impact figures on chrome-nickel steel:

No. of grains per sq. mm.	Izod figure
2103	60
2762	54
1527	37
914	4
875	10
1256	9

<sup>20</sup> *J. Am. Inst. Metals* 11, 318

<sup>21</sup> The "eutectic drop" or drop in the melting point of a mixture of two substances, is a phenomenon of widespread occurrence outside of the field of metals, and resembles the lowering of the freezing point of water by substances dissolved in it. Thus mixtures of fats or of fatty acids show the phenomenon (see Lewkowitsch, 5th ed., Vol. 1,



alloy. Speaking of one of the best known alloys, brass, Sir W. Roberts-Austen<sup>22</sup> says:

"It is almost impossible by mechanical means to detect the separate ingredients in such an alloy; we may cut or file or polish it without discovering any lack of homogeneousness. But it is not permissible to call brass a chemical compound, for we can largely alter its percentage composition without the substance losing the properties characteristic of brass; the properties change more or less continuously, the color, for example, becoming redder with decrease in the percentage of zinc, and a paler yellow when there is more zinc. The possibility of continuously varying the percentage composition suggests analogy between an alloy and a solution and A. Matthieson (*Phil. Trans.*, 1860) applied the term 'solidified solution' to alloys. Regarded as descriptive of the genesis of an alloy from a uniform liquid containing two or more metals, the term is not incorrect, and it may have acted as a sign-post towards profitable methods of research. But modern work has shown that, although alloys sometimes contain solid solutions, the solid alloy as a whole is often far more like a conglomerate rock than a uniform solution."

As Zsigmondy has pointed out<sup>23</sup> the original definitions of "solution" are based on the concept "homogeneity"—solutions were

p. 116) and Schaffgotsch (*Pogg. Ann.*, 102, from Carnelly, "Melting and Boiling Point Tables," 1885, Vol. 1, p. 46) gives the following:

Per cent. $\text{KNO}_3$	$\text{NaNO}_3$	M. p. of mixture
100	0	338.3
90	10	317
80	20	280
70	30	250
60	40	230
54.3	45.7 $\text{KNaO}_3$	225.6
50	50 $\text{NaNO}_3$	229
40	60	244
30	70	262
20	80	281
10	90	298
0	100	313

Wood's fusible metal which melts at 65°, is composed of:

- 4 Bismuth
- 1 Cadmium
- 2 Lead
- 1 Tin

This seems to be a good illustration of cumulative protection.

<sup>22</sup> *Encyclopedia Britannica*, Vol. 1, p. 704

<sup>23</sup> "Colloids and the Ultra-microscope," p. 1

supposed to be homogeneous. Thus the Standard Dictionary defines solid solution as "a homogeneous non-crystalline, solidified solution." But successive series of heterogeneity underlie substances that appear homogeneous to the eye or even to the most powerful microscope.

At present, electrons, positive and negative, are the only things not known to be heterogeneous. Atoms are complexes of positive and of negative electrons; molecules are complexes of atoms; and colloidal particles are aggregates (crystalline or amorphous as the case may be) of molecules. But all of these being smaller than a wave length of light, cannot be resolved by the microscope. Sir William Ramsay<sup>24</sup> clearly saw that there is a gradual progress from visibly heterogeneous suspensions to apparently homogeneous solutions, but it was not until the invention and development of the ultramicroscope by Zsigmondy and Siedentopf (about 1903) that this could be visually demonstrated. Still more recently the X-ray spectrometer of Bragg, by utilizing wave lengths of only a few Ångstrom units ( $1 \text{ Å} = \frac{1}{10} \mu\mu = \frac{1}{10,000} \mu = \frac{1}{10,000,000} \text{ mm.}$ ), has actually located the relative positions of atoms in many crystals.<sup>25</sup>

In the great majority of cases solidified alloys show a structure easily resolvable by a low powered microscope. If the chilling has been rather slow, etching agents reveal crystals, but drastic chilling may result in crystals so fine as to be colloidal. Between the visible crystals and the colloidal aggregates come the crystallites, a term borrowed from the petrologist. Thus J. S. Flett states:<sup>26</sup> "In media which, on account of their viscosity,

<sup>24</sup> *Chem. News*, 65, 90 (1892)

<sup>25</sup> In make up, visible particles of matter may show all the following degrees of complexity:

Group		Order of complexity	May be photographed by or made visible by
1	Electrons	0??	Ionized particles X-ray spectrometer X-ray spectrometer X-ray spectrometer Ultramicroscope Ultramicroscope Microscope
2	Atoms	1	
3	Molecules	2	
4	Molecular Groups	3	
5	Primary Colloidal Particles	4	
6	Secondary Colloidal Particles	5	
7	Visible Particles	6	

<sup>26</sup> *Encyclopedia Britannica*, 11th ed. Vol. 7, p. 568

offer considerable resistance to those molecular movements which are necessary for the building and growth of crystals, rudimentary or imperfect forms of crystallization very frequently occur. Such media are the volcanic rocks when they are rapidly cooled, producing various kinds of pitchstone, obsidian, etc.... Crystallites may also be produced by allowing a solution of sulphur in carbon disulphide mixed with Canada balsam to evaporate slowly, and their development may be watched on a microscope slide. Small globules appear (globulites), spherical and non-crystalline (so far as can be ascertained). They may coalesce or may arrange themselves into rows like strings of beads—margerites—(Gr. *μαργαριτης*, a pearl) or into groups with a somewhat radiate arrangement—globospherites. Occasionally they take elongated shapes—longulites or baculites (Lat. *baculus*, a staff). The largest may become crystalline, changing suddenly into polyhedral bodies with evident double refraction and the optical properties belonging to crystals. Others become long and thread-like—trichites (Gr. *θρ' ξτριχος*, hair)—and these are often curved, and a group of them may be implanted on the surface of a small crystal. All these forms are found in vitreous igneous rocks. H. P. J. Vogelsang, who was the first to direct much attention to them, believes that the globulites are preliminary stages in the formation of crystals."

#### THE BEHAVIOR OF SULPHUR

Since it seemed probable that in the experiment above mentioned the Canada balsam would function as a protector or crystal inhibitor, a slide was prepared as indicated, and submitted to ultramicroscopic examination. On searching the field under low power (Leitz objective No. 3), a place was observed where the solution had been rubbed out rather thin, in which appeared numerous crystals and crystallites surrounded by a vacant space outside of which was a considerable area of unoriented ultramicros. <sup>27</sup> When the high power objective (Leitz No. 6) was focussed on the spot, the unoriented ultramicros were more clearly seen, but since they were apparently smaller than the wave length of light, that is less than about  $\frac{1}{4}\mu$ , they showed only diffraction discs and could not be resolved. Therefore, though they were colloidal, it is not

<sup>27</sup> These ultramicros were mainly in microscopically visible aggregates.

possible to say if in their own structure they are amorphous or crystalline. The latter seems probable, since the crystals or crystallites seemed to be formed of ultramicros arranged in orderly fashion, even if the outer layers showed deficiencies and superfluities of ultramicros.

Furthermore there were vacant areas surrounding the crystalline forms, indicating that they had been deprived of their ultramicros by the growing crystal nucleus. A second slide was therefore made without a cover glass on which the solution of sulphur was rubbed out quite thin so that the carbon disulphide evaporated very rapidly. It showed large areas of ultramicros, surrounding or bordering crystal areas, each crystal or crystal group being surrounded by an area free from ultramicros. Under high power, ultramicros were seen adhering to crystals, as though they had been drawn there by surface forces and had either been unable to find proper lodgment or else had been prevented from amalgamating with the mass of the crystal because of chilling, or evaporation of the solvent, or interference of the protector.

In some places aggregations of ultramicros were seen, having the appearance of incipient crystallization; for they were grouped into the semblance of order, and vacant spaces were beginning to appear between them. Photographs of this slide are presented herewith.

From the colloid point of view, we are justified in considering binary alloys as dispersions of one metal in another, unless the conditions are still further complicated by the formation of eutectics, of allotropes, or of definite chemical compounds. New phases forming, may be considered either as additional dispersed substances, or else as modifiers of the dispersion medium. In general it seems reasonable to regard as part of the dispersion medium, whatever acts with it, and to regard as the dispersed phases those which first aggregate or separate out. Since solubilities and the stability of chemical compounds and allotropes vary with temperature, various substances may separate successively upon cooling, and form a series of dispersed substances whose effect in the colloidal zone may be registered at different times, thus yielding a cumulative effect.

The difficulty of submitting natural phenomena of this class to exact mathematical analysis, is obvious from the fact that

mathematicians have so far been unable to formulate the behavior of three bodies acting under the relatively simply expressed law of gravitation. Upon alloying carbon with iron to make simple steel, we have to consider at least two allotropes of iron, carbide of iron with varying solubility, and perhaps free carbon. The complexity of this comparatively simple system is obvious from the enormous literature regarding it, so that we can well imagine that it is not easy to understand the behavior, under varying conditions, of alloy steels containing several metals in addition to iron and carbon.

Nature often produces very complicated effects by the simultaneous action of comparatively simple laws; and among the factors controlling the behavior of alloys the following colloidal principles seem to exert a marked influence:

(a) *Adsorption*—a phase on becoming colloidal, may, because of its increased surface and reduced kinetic activity, form adsorption compounds of more or less limited life.

(b) *Protection*—phases, added or formed, may tend to delay or inhibit the aggregation or crystallization of others. There may be simple protection, auto-protection, or cumulative protection.<sup>28</sup>

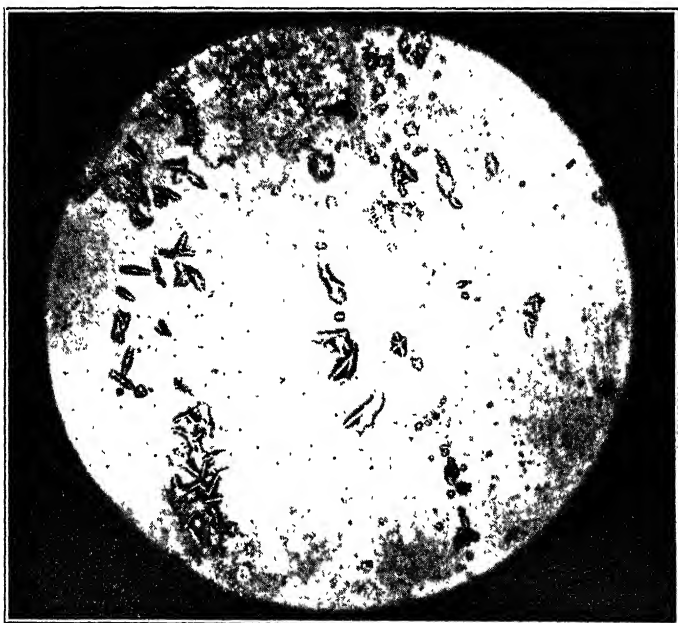
(c) *Zone of Maximum Colloidalilty*—Particles or aggregates smaller than the colloidal range have too great a kinetic activity to remain attached to any group, while those larger than the colloidal range are comparatively inactive. There is therefore within the colloidal range, a zone wherein the effects of subdivision or dispersion are registered to a maximum.

(d) Change of viscosity of the dispersing phase due to additions, impurities or temperature changes.

To illustrate these principles, let us consider in detail some of the phenomena of steels, first reviewing the behavior of pure iron, which will form a background.

*Pure Iron*—Pure iron freezes at about 1505°C., and as it cools further, shows a large evolution of heat at about 900° (thermal arrest point Ar<sub>3</sub>) and a smaller evolution of heat at about 780° (thermal arrest point Ar<sub>2</sub>). Metallurgists agree that above 900°, the iron exists as a non-magnetic allotrope,  $\gamma$  iron; while below 780°, it exists as a magnetic allotrope of different crystalline form,  $\alpha$  iron or ferrite. It was generally

<sup>28</sup> J. Alexander, *J. Ind. Eng. Chem.*, **15**, 283 (1923)



Sulphur crystallizing from CS<sub>2</sub> in the presence of Canada balsam.  
Showing intermediate forms.



thought<sup>29</sup> that between these temperatures the iron exists in a third allotropic form,  $\beta$  iron, having the same crystal form as  $\alpha$  iron, but being non-magnetic like  $\gamma$  iron. C. Benedicks,<sup>30</sup> however, thinks that the evolution of heat at 780° does not represent the transformation of a  $\beta$  allotrope to  $\alpha$  iron, but is consequent upon the final disappearance of persistent  $\gamma$  iron molecules from the metal.

Since the X-ray spectrometer shows that there are only two types of crystal groupings of iron atoms to form crystals, the face-centered lattice for  $\gamma$  iron and the body-centered lattice for  $\alpha$  and  $\Delta$ <sup>31</sup> iron, Benedicks' view seems to be the correct one. Between 900° and 780°, iron is an allocolloid, a dispersion of  $\alpha$  iron in  $\gamma$  iron forming an  $\alpha$ - $\gamma$  adsorption compound, whose break-up into the more completely oriented  $\alpha$  iron sets free the comparatively smaller amount of heat at the point  $Ar_2$ .

The view that the so-called " $\beta$  allotrope of iron" is an adsorption product of  $\alpha$  and  $\gamma$  iron, accounts for the following facts: (1) " $\beta$ -iron" has the same crystal form as its dominant partner,  $\alpha$  iron, but is not magnetic as is  $\alpha$  iron, because magnetism evidently depends on a certain spacing and regularity of molecular orientation.<sup>32</sup> (2)  $\gamma$  iron dissolves iron carbide (cementite), whereas  $\alpha$  iron and " $\beta$  iron" do not; whatever  $\gamma$  iron exists in the " $\beta$ " zone, is adsorbed by or is in some kind of loose combination with the dominant  $\alpha$  iron, and is not free to exert any solvent action on iron carbide; (3) on heating iron, there is an increase in strength at about 780°, when the formation of some  $\gamma$  iron results in the formation of some of the  $\alpha$ - $\gamma$  adsorption compound, which increases the free surface and strength of the system; (4) the structure of " $\beta$  iron" is finely acicular, indicative of crystallization in the presence of a colloid.

### STEEL

With simple steel, which is essentially iron containing small percentages of carbon, we have a new complication introduced, for the iron carbide formed, though quite soluble in  $\gamma$  iron, is not soluble in  $\alpha$  iron.

<sup>29</sup> H. M. Howe, "Metallography of Steel and Cast Iron," also W. Rosenhain, "Introduction to Physical Metallurgy," p. 170

<sup>30</sup> *J. Iron Steel Inst.*, No. 2, 1912

<sup>31</sup>  $\Delta$  iron is a recently accepted 3rd allotropic form of iron, stable about 1400°

<sup>32</sup> The Haeussler alloys are magnetic, though their individual constituents are not



Low carbon steel, *e. g.*, with 0.2 per cent. of carbon (which dissolves in the liquid iron as  $\text{Fe}_3\text{C}$ ), shows its  $\text{Ar}_3$  point at about  $840^\circ$ , the influence of the cementite causing a drop in the temperature at which the  $\alpha$ - $\gamma$  dispersion forms. There is another thermal arrest point at  $750^\circ$ , when the  $\alpha$ - $\gamma$  allo-colloid decomposes into  $\alpha$  iron, the steel then consisting of  $\alpha$  iron holding in dispersion an adsorption compound of iron carbide and  $\gamma$  iron. When the temperature falls to a little below  $700^\circ$ , the  $\gamma$  iron remaining suddenly is converted into  $\alpha$  iron, and the cementite ( $\text{Fe}_3\text{C}$ ), being left without any solvent or protector, forms aggregates. These two changes occur simultaneously, and account for the evolution of heat at this point,  $\text{Ar}_1$ .

The adsorption compound between  $\gamma$  iron and cementite is what causes some of the  $\gamma$  iron to be carried over though the so-called " $\beta$  iron" zone to the eutectoid point ( $\text{Ar}_1$ ). But a small amount of carbon means a large percentage of cementite; thus 0.5 per cent. C. means about 7.5 per cent.  $\text{Fe}_3\text{C}$ , and 0.9 per cent. C. means 13.5 per cent.  $\text{Fe}_3\text{C}$ . Therefore as the carbon content increases, the allotropic transformation of the iron at  $\text{Ar}_2$  becomes of lesser and lesser importance, until with eutectoid steel (0.9 per cent. C.) we find a single thermal arrest point at which it actually glows.

This phenomenon, called *recalcescence*, is due to the breakdown of an extensive metastable system or dispersion of cementite in  $\gamma$  iron. Two delayed transformations occur simultaneously, all the iron transforming from  $\gamma$  into  $\alpha$  form, and the cementite, freed from the dispersing action of the  $\gamma$  iron exhibits its powerful aggregation tendency by forming groups of its own.

These phenomena are well shown in the accompanying diagram of the cooling curves of iron and iron-carbon alloys, taken from H. C. H. Carpenter's paper on "The Hardening of Steel."<sup>33</sup>

Now the size of the groups which the released cementite will form in any particular case, depends upon a number of factors, chief among which are the speed of cooling, and the presence of impurities in or additions to the steel.

The speed of cooling regulates the time within which the iron dispersion medium becomes so viscous that the aggregation tendencies of the cementite are prevented from establishing

<sup>33</sup> *Engineering*, 107, 341, March 14, 1919

themselves. The quicker the chilling, the finer the dispersion of the cementite when the metal sets hard. In unquenched steel it usually appears as fine plates or fibrils interspersed with  $\alpha$  iron (ferrite), yielding the finely laminated structure known as pearlite, for the reason that under proper illumination, it exhibits the iridescent luster of mother-of-pearl.<sup>34</sup> The lamellae

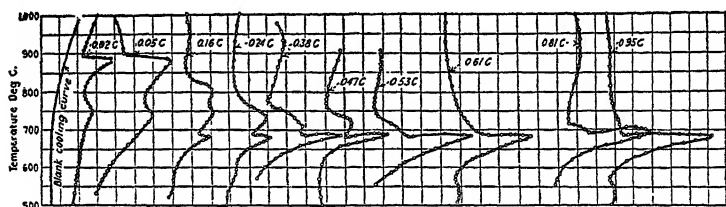


Fig. 2.—Changes in thermal arrest points of steels with increasing carbon content.

in pearlite tax the highest power of the microscope for their successful resolution, and the iridescence recalls that of a finely ruled diffraction grating.

Again substances like silicon, manganese, tungsten, etc., which increase the viscosity of the dispersing iron, and which perhaps adhere to or form adsorption compounds with the cementite, also delay its aggregation. This aggregation takes a measurable time; and anything increasing the viscosity of the dispersion medium, whether it be an impurity, an intentionally added substance, or simply a drop in temperature, may cause a time lag in the process, so that when the metal becomes too rigid to allow aggregation to proceed further, the cementite has formed smaller groups than would have otherwise been the case.

On the other hand, by cooling steel very slowly, or by reheating it for a long time at about 900°, the cementite groups up into relatively large balls, the dispersing ferrite at the same time forming larger crystals. The behavior of such steels is highly unsatisfactory in practice.<sup>35</sup>

Metallurgists recognize between the extreme of aggregation, and the apparently "homogeneous" dispersion of cementite in freezing iron, the following structures:

<sup>34</sup> A close imitation of mother-of-pearl has been produced by L. Clement and C. Rivière (See *Chimie et industrie*, 8, 782 (1922), by allowing calcium carbonate to form in gels

<sup>35</sup> Rosenhain, *loc. cit.*, p. 278

*Austenite* (named after Roberts-Austen)—White, apparently structureless  $\gamma$  iron solid solution, which is preserved as such by quenching or by the presence of some alloying element, such as manganese. It is commonly regarded as a solid solution, but probably is an extremely fine colloidal dispersion.

*Martensite* (named after Martens)—The hardest constituent of hardened steels, representing the first step in the aggregation of the  $\gamma$  iron dispersion. It usually shows an acicular structure, and may be so fine that this structure is revealed only with the utmost difficulty. Such "structureless" martensite is sometimes termed "hardenite."

*Troostite* (named after Troost)—This dark-etching constituent has rounded or woolly outlines, reminding one of the shape of globulites or crystal-druses. It is found particularly in hypo-eutectoid steels at the edges of martensite grains, especially where they border on ferrite. In fact, by regulated cooling or tempering, martensite can be converted into troostite. Benedicks<sup>36</sup> regards the carbide in troostite as being in colloidal dispersion; he calls troostite "a solid colloidal 'solution' of cementite in iron (a solid cementite ferrosol)."

Using cylindrical test pieces of 1 per cent. carbon steel 50 mm. long and 6.5 mm. in diameter, Benedicks reported the following results:

Temperature of steel in °C	Time of cooling to 100° C	Results of microscopic examinations
950	3.07 seconds	Only martensite
848	4.32 "	" "
750	4.11 "	" "
715	5.33 "	Martensite with traces of troostite
695	6.2 "	" " " " "
725	9.5 "	All troostite

To lengthen the cooling time of the last specimen it was wound with a piece of iron 1 mm. wide, increasing its weight from 12.3 to 27.5 grams.

These results of Benedicks indicate the extreme rapidity with which, under favorable conditions, aggregations may occur in steel.

*Sorbite* (named after Sorby)—This is described by W. Rosenhain<sup>37</sup> as follows:

<sup>36</sup> *Kolloid-Z.*, 7, 290 (1910)

<sup>37</sup> "Introduction to Physical Metallurgy," pp. 182-184

"When the rate of cooling is further lessened or the temperature of reheating is further increased, the steel is permitted to progress somewhat further toward the final state of ferrite plus cementite. Instead of the troostite described above we find a constituent still devoid of any visible detailed structure under the highest magnifications, but not etching to such a deep color as troostite and without the peculiar rounded outlines. This is often called 'sorbite,' but it may be regarded as simply a variety of pearlite in which the constituents are so finely divided that they cannot be microscopically separated. The dividing line between sorbite and pearlite, indeed, is simply a question of microscopic resolving power."

*Pearlite*—This iridescent and microscopically resolvable dispersion of cementite ( $\text{Fe}_3\text{C}$ ) has been already described above.

Interesting evidence of the colloidal nature of the cementite in properly quenched tool steel, is given by its behavior with solvents of iron, acids for example. Whereas annealed steel leaves a residue of carbide, hardened steel gives no residue, but forms instead a complicated mixture of hydrocarbons, both liquid and gaseous. This indicates that the particles of cementite,  $\text{Fe}_3\text{C}$ , in hardened tool steel are so small that acid readily attacks them, liberating carbon in so fine a condition of dispersion that the nascent hydrogen may combine with it.<sup>38</sup>

The variety of hydrocarbons produced under these circumstances reflects rather the great diversity of carbide particles in point of size, and not the existence of a number of different carbides or "chemical compounds" invented to explain an otherwise simple phenomenon. By grinding iron carbide into colloidal dispersion, I hope to be able to reproduce the formation of hydrocarbons.

Another bit of evidence indicating that in hardened steel the cementite is mainly colloidal, is given by the existence of a zone of maximum hardness, which corresponds with a zone of maximum colloidity or optimum dispersion.<sup>39</sup> Thus austenite is a finer dispersion than martensite, but is softer; while troostite,

<sup>38</sup> That colloidal dispersion causes great chemical activity is well known. While even fine precipitated sulphur will not affect silver salts in the cold, and does so only partly on boiling, colloidal sulphur reduces them energetically even at room temperature. Fine phosphorus exposed to air by the evaporation of its solvent ( $\text{CS}_2$  or ether) takes fire spontaneously, as does the finely divided lead produced by heating lead tartrate in a tube

<sup>39</sup> J. Alexander, *J. Am. Chem. Soc.*, **43**, 434 (1920)

sorbite, and pearlite are progressively coarser dispersions than martensite, but are likewise softer. Jeffries and Archer<sup>40</sup> believe that this phenomenon, an analogue of which occurs in the alloy duralumin, is due to the fact that the hard particles of the dispersed phase act as *keys*, preventing any motion along the cleavage or slip planes as a whole. While this mechanical comparison may appeal to engineers, the action of surface forces, together with the fineness of crystal grain which minimizes the length of the slip planes, are quite sufficient to account for the phenomena observed.

The enormous power of these surface forces is shown by the results of some experiments privately communicated to me by P. Scherrer of Zurich. He coagulated unprotected gold sols with electrolytes, and by X-ray examination found that the tiny ultramicros (which were about  $2\ \mu\mu$  in diameter and showed a crystalline gold space lattice) practically fused together into homogeneous crystals of larger size. Even soft substances, if finely dispersed, will produce great increase in hardness. Thus a few per cent. of oil added to whiting makes a firm putty when ground in with it. And S. U. Pickering<sup>41</sup> made an extremely stiff mass by emulsifying 99 per cent. of petroleum oil in 1 per cent. of soap water.

#### ALLOY STEELS

The behavior of the so-called alloy steels shows the powerful effect of the added metals, which, by increasing the viscosity of the dispersing iron or acting as protectors or dispersors to the dispersed phases, tend to maintain the degree of subdivision conducive to hardness. Thus Mauer showed that the addition of manganese to steel retards the aggregation of the cementite to such an extent that ordinary slow cooling yields martensite. With larger quantities of manganese, austenite is formed. With high speed steels harmful aggregation does not occur even at red heat.

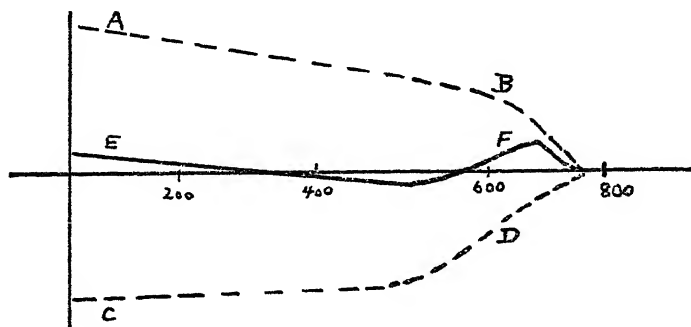
#### STEPPED TRANSFORMATION IN STEELS

The aggregation of cementite takes time and there is always a time lag in the process. Consequently when carbon steel is

<sup>40</sup> *Chem. Met. Eng.*, **24**, 1065 (1922)

<sup>41</sup> *J. Chem. Soc.*, **91**, 2002 (1902)

rapidly cooled, the  $A_1$  transformation takes place at a lower temperature than when it is slowly cooled. This drop increases with the speed of chilling until it reaches about  $600^\circ\text{C}.$ , when



AB = tendency curve; CD = resistance curve; EF = observed resultant.

Fig. 3.—Aggregation-viscosity curves, with resultant showing aggregation inhibited between about  $600$ – $300^\circ$ .

still more drastic chilling lowers it discontinuously to about  $300^\circ\text{C}.$  or less.

This *stepped  $A_1$  transformation*, as it is known, is beautifully explained by Kôtarô Honda<sup>42</sup> who shows that it is due to the fact that in the inhibited zone the viscosity of the dispersion medium is sufficient to stop the aggregation of the cementite, but that below this zone the aggregation forces of the cementite become so powerful that they then overcome the resistance of the iron, notwithstanding the fact that its viscosity has likewise increased by cooling. The following curve, taken from Honda's paper shows how two factors operating at various rates over a temperature range, may cause puzzling results, unless their effects can be separately analyzed.

AB is the transforming tendency or aggregating curve, plotted positively; EF is the resultant, which represents the extent to which the tendency is able to establish itself.

#### DISCUSSION ON J. ALEXANDER'S PAPER

#### THE COLLOIDAL STATE IN METALS AND ALLOYS

J. H. MATHEWS: What Mr. Alexander had to say concerning

<sup>42</sup> Advance proof, *Iron Steel Inst.*, May, 1922

the transition state from the crystalloid to the colloidal condition reminds me of a certain very interesting laboratory experiment which, by the way, has nothing to do with alloys. As you all heard the other day, sugar is soluble in pyridine. If one takes a saturated solution of sugar in pyridine and puts a drop of it under a microscope and then allows a stream of benzol to diffuse in slowly, the sugar will be thrown out of solution. Now if one observes this under a high-powered polarizing microscope one will see something that is extremely interesting. At first minute points form, and then they gradually grow and grow and present a globular appearance. Then suddenly one sees flashes of light here and there due to crystallization. It shows very nicely the transition stage from the molecular through to the crystalline condition. One sees at first tiny points; they grow and grow, and then the crystalline formation appears. I have never examined this under the ultramicroscope but I think it would be a very interesting thing to do. Perhaps one could carry the observation of the process back farther by the ultramicroscope. Quincke would have been pleased with this experiment for, as you will recall, he contended that all precipitates at the moment of their formation are liquid and that crystallization appears later.

H. N. HOLMES: To what extent do the principles of emulsification enter if at all? Take one metal that does not dissolve another, just as we have in liquids under ordinary temperature conditions, and then have present another substance acting as an emulsifying agent; has that been done?

J. ALEXANDER: As a matter of fact that is a common practice. I have tried to bring that out in my paper, explaining where various metals help keep each other dispersed.

H. N. HOLMES: I do not mean emulsification by preventing the increase of the size of the particles upon cooling, but by mechanical beating.

J. ALEXANDER: Isn't it the Patterson process for separating silver from zinc that depends upon gravitation? The reason I didn't stress many of the facts regarding metals particularly is because I thought you were more interested in colloid chemical principles; and I have so used my limited time here. Those who are interested in the purely metallurgical side can read the paper at leisure.

R. NEWTON: I would like to ask one or two questions. I will perhaps merely display my ignorance, but I should like to ask Mr. Alexander if he really believes in that table of boiling points there on the board. I have been under the impression that these substances have long ago been carefully purified. The other question I would like to ask is in reference to those curves on this board here. I should like to have some information as to what brings about the break in that curve in the zone of maximum colloidalilty. I understand they depend upon the fineness of subdivision of the particles. Why does that break just at that particular point?

J. ALEXANDER: In reply to your first question, I might say that the paper from which I took these figures regarding boiling points is a paper by Prof. H. B. Baker and I am quite sure that the Chemical Society of London would never have permitted him to publish such startling data unless he had satisfied them that he had sufficient data for substantiating his material.

Replying to your second question, the break in the curve is not a cusp. It is a zone rather than a point of inflection, and will undoubtedly vary with different substances, and under different conditions. To illustrate, a rope of sand is not coherent because of deficiency in free surface. A rope of fine clay is coherent, because the free surface is large but the kinetic activity of the particles is not great enough to disrupt the bond. Silicate of soda, which consists mainly of silica dispersed in alkali, makes a fluid solution, because the kinetic activity of the particles prevents the formation of coherent groups.

F. E. CLARK: Were not those experiments carried out as the result of an accident; did not Dr. Baker prepare that stuff and then was he not called away to war? Then after the war when he returned to it, he found in the case of alcohol that the boiling point was almost double; and that result is due to several years' standing.

J. ALEXANDER: Yes, it is mentioned over there on the black board—the number of years that they stood.

F. E. CLARK: Did he make any experiments to confirm these?

J. ALEXANDER: That is just what he did. He started to make these experiments and then he was called away to war



and did not come back to them for many years. I think I mentioned that at the outset.

F. E. CLARK: I was not here when you started, perhaps.

E. D. FAHLBERG: I believe Dr. Alexander has written on this before, as to what effect addition agents have upon crystallization. In the manufacture of tungsten a certain amount of thorium is used. However, it is a very small amount, about 1%, as that amount will prevent excessive crystal growth. A further increase of  $\text{ThO}_2$  (3-4%) will prevent all crystal growth. That is, the grain growth decreases with that amount of  $\text{ThO}_2$ , but on increasing the  $\text{ThO}_2$  content to  $4\frac{1}{2}\%$  an enormous increase in grain growth takes place. I would like to hear an explanation of that.

J. ALEXANDER: I never have heard those facts, but from what you say I would gather that the following is the case: In the case where small percentages of thorium are added to the tungsten, thorium oxide—is it oxide?

E. D. FAHLBERG: Yes.

J. ALEXANDER: Is that soluble in tungsten?

E. D. FAHLBERG: I don't believe so.

J. ALEXANDER: Does it disperse?

E. D. FAHLBERG: It forms small spherical globules.

J. ALEXANDER: Does it disperse thoroughly in the tungsten?

E. D. FAHLBERG: I imagine it does as the size of these globules does not vary to any marked degree.

J. ALEXANDER: Without knowing all the facts I do not think I can answer. A possible explanation is this: In the case of small percentages of thorium you have the thorium acting as a protector. In the case of the larger percentages, its viscosity effect may come into play. It may increase the viscosity of the whole mass, just as tungsten does in alloy steels. I do not think it would be fair to attempt to give an explanation of such a phenomenon without knowing all the facts, and investigating them. I only offer this as a possible suggestion.

R. A. GORTNER: Might not that be an action of the emulsifying agent in two metals? You can put a certain amount in it and yet you get no increase in the dispersion of the one material in the other, and this looks as though it might be merely the application of the emulsifying agent.

## COLLOID PROPERTIES OF RUBBER AND COMPOUND INGREDIENTS

BY ELLWOOD B. SPEAR

The purpose of this article is to discuss, briefly, the experimental basis upon which the theories of the structure of raw and vulcanized rubber rest. In addition to this, a new theory is presented for the reinforcing action of compounding materials which is in harmony with theories that have been propounded in the case of other colloid systems. The need of fundamental colloid research on rubber is pointed out and some specific problems are suggested.

The splendid researches of Harries and others have thrown considerable light on the structure of the caoutchouc molecule. In a recent publication<sup>1</sup> Harries suggests  $(C_5H_8)_8$  as the formula for caoutchouc, where 32 carbon atoms form a ring compound. Without detracting in the slightest degree from this excellent work, it must be admitted that rubber is an excellent example of a substance in the colloidal state and that colloids are not one component systems as far as their physical properties are concerned. While  $(C_5H_8)_8$  may be the formula for the ultimate molecule of caoutchouc, it is probable that the former should be written  $[(C_5H_8)_8]_x$ , where  $x$  may have different values.

As is well known, the latex is obtained from certain trees in the form of a milk. Thirty to thirty-five per cent. of the total weight of the latex consists of colloidal globules of caoutchouc. These globules have a diameter varying from  $0.5\mu$  to  $3\mu$ . It is generally conceded that the outer layer of these globules consists of a skin of protein material.<sup>2</sup>

The material is coagulated by several methods which could be anticipated in part by anyone familiar with colloidal sols. Some of these methods are extremely interesting but space will not permit dealing with this side of the subject in exhaustive detail. The chief item of interest for the purposes of this article is the consideration of what occurs when these colloidal particles are brought together to form an elastic coagulum.

<sup>1</sup> *India Rubber World*, **66**, 679(1922)

<sup>2</sup> This outer skin in the case of *Funtumia Elastica* consists of peptone instead of protein

Do the particles come together by surface contact only, or is the protective film destroyed so that the caoutchouc inside the particles flows together to form a single phase such as is the case for instance when a benzol emulsion in water separates into two layers, benzol and water. It is also possible to imagine, of course, that some of the globules remain intact, whereas others are destroyed and go to form a matrix of caoutchouc. In that case, we should have globules with their protective films as the disperse phase and a continuous phase or disperse medium consisting of caoutchouc.

It has been suggested by Pratt<sup>3</sup> that during the coagulation, a large part at least of the globules of caoutchouc remain unaltered and, therefore, the individual entities of the latex and the coagulum are identical. This view is supported, it is claimed, by some of Pratt's recent work,<sup>4</sup> where he has been able to redisperse raw gum into an aqueous medium by the aid of certain protective colloids. The dispersion is made by dissolving the raw rubber in benzol to which oleic acid and ammonia have been added.

By this procedure, a suspension is obtained of such stability that the benzol may be removed by a current of air or by evaporation caused by gentle heating. Although the suspension is not identical with the original latex, it exhibits, nevertheless, many properties that are not dissimilar. For instance, the globules in this artificial latex, if observed under the microscope, appear to have approximately the same diameters as those in the "mother" liquid from the tree. These particles may be coagulated into an elastic mass and may be redispersed in a suspending medium. The process is capable of repetition any number of times.

The evidence in favor of this theory is not very convincing for although discrete particles may be seen in freshly coagulated latex by means of the microscope, they disappear entirely as soon as the coagulum is masticated. Moreover, it is altogether probable that most of the protein film is decomposed during maturation and that the original particles at least lose their identity.

The theory of Pratt is not contrary in some respects to those

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<sup>3</sup> *India Rubber World*, **67**, 212 (1923).

<sup>4</sup> *India Rubber World*, **67**, 213-15, 291-93, 488-90 (1923)

proposed by several others<sup>5</sup> in which it is assumed that in the coagulum there are particles somewhat spherical in shape suspended in the medium of the same analytical composition but differing in physical constitution. In other words, we have here a case of a single chemical substance as far as chemical analysis is concerned in at least two different physical states. It is quite possible, of course, that there are many different physical states in this system. From this point of view, raw rubber is therefore, a two-component, or possibly a multi-component, system physically without taking into consideration the resin and proteins that may be present. According to this theory, these particles are supposed to consist of a tough elastic outer layer and an interior substance which has a somewhat greater plasticity, or possibly a viscosity resembling a viscous liquid. If it be granted that some of the globules in the latex are broken during coagulation and the substance from the interior of the globules goes to form the matrix of the coagulum in which the spherical bodies are suspended, all these theories have much in common.

There is one vital difference however, that must not be overlooked. According to the theory of Pratt, the particles in the coagulum have the same protective coating of protein that they had in the latex, whereas the last mentioned theories would predicate that the elastic film around the particles is composed chiefly or entirely, of caoutchouc which is more highly polymerized than that of the matrix. Neither of these theories would preclude the superimposition of a more or less definite orientation of the disperse phase in the matrix. The persistence of a decided "grain" in milled rubber is evidence in favor of this point of view as will be seen later on in this article.

The theories of Nägeli, Bütschli and their modern modifications as applied to the structure of rubber have been suggested from time to time. Furthermore, the micellar theory, as expounded by McBain and others for the constitution of soaps, may very well obtain in the case of rubber. It is natural that the colloid chemist should favor these theories rather than the more radical pictures outlined above.

<sup>5</sup> Bjerken, *Ann. phys.*, **43**, 808-31 (1891); Schiller, *ibid.*, **35**, 931 (1911); A. Mallock, *Proc. Roy. Soc. (London)* **46**, 233-49 (1889); Cheneveau and Heim, *Compt. rend.*, **152**, 320 (1911); Fessenden, *J. Franklin Inst.*, **142**, 207-9 (1896); R. W. Lunnon, *India Rubber J.*, **62**, 831-2 (1921)

## EFFECT OF HEAT AND MECHANICAL MANIPULATION UPON UNCURED RUBBER

While rubber is being milled, it is lengthened circumferentially around the roll, spread out somewhat along the roll at right angles to the circumference and thinned in the direction normal to the roll. For convenience, we will speak of these directions as length, width, and thickness, respectively. If the milling has not been carried on too long and at too high a temperature, the sheet of raw rubber will crawl in such a manner after it is cut off the roll, that it will become much shorter, widen slightly and thicken considerably. It is obvious from this that the mass does not behave exactly as do most plastic solids such, for example, as a block of paraffin. On the other hand, if a mass of raw rubber is pressed between two plates slowly enough it does not show any appreciable tendency to recover its original shape. It exhibits, therefore, normal plastic properties.

Attempts have been made to explain this behavior on the basis of the structure outlined above. If we have a liquid or a very plastic solid enclosed in an elastic membrane and we change the dimensions of the diameters of the spheres in the three directions as we probably do in milling, there will be an effort on the part of the mass to allow the elliptically shaped globules to return to the spherical shape, and hence, the rubber should crawl most in a direction opposite to that in which it has been most distorted, *i. e.*, circumferentially around the roll.

As the globules are forced farther and farther from the spherical toward the elliptical shape, the interior liquid, or solid, of high plasticity, will be under a constantly increasing compression. The larger the force of compression, the greater will be the resistance offered by the mass to further distortion. It is clear from these considerations, that as long as the external films of the globules, be they protein or polymerized caoutchouc, are not ruptured, the compression of the internal liquid will cause the mass to make vigorous efforts toward regaining its original shape. In technical terms, cured rubber will snap back or be lively, while raw rubber will have a tendency to recover from the effect of the distortion.

Quite otherwise will be the effect of applied pressure, however, if sufficient time is allowed for the mass to adjust itself to the

new conditions. Here the matrix will make way for the spheres so that the latter will not be forced out of shape to any very great degree. In other words, if the matrix is given time to flow raw rubber behaves as a normal plastic solid but, if the distorting forces are applied too rapidly, the mass will exhibit elastic properties.

The question might well be asked at this point, do not high temperatures and milling tend to break down these hypothetical globules or cellular formations? The answer is decidedly "yes, they do." High temperatures for some time or a long period of milling, increase the plasticity and decrease the elasticity until rubber behaves like an ordinary plastic solid. When rubber is badly overmilled, it shows almost no tendency to crawl. Moreover, it is not possible by any method of curing to obtain as good quality from over-milled rubber as it was from the original before the severe and prolonged masticating process. This would indicate strongly that long heating or over-milling will break down some sort of complex in the rubber which is essential for high quality.

If the quality of the rubber depends to any appreciable extent upon the existence of these globular or cellular particles, then any severe mastication should tend to rupture a large portion of the globules. As a consequence, we should have a mass consisting of more matrix and less globules or cells. In other words, severe mastication should tend to destroy or degrade the rubber. This is not only in accordance with the facts, but is such an important factor in technical operations that great care must be exercised not to over-mill the rubber while mixing in compounding ingredients.<sup>6</sup>

#### VULCANIZATION

It is generally conceded among chemists that sulfur unites chemically with the caoutchouc during the process of vulcanization. It is also thought that aggregates are built up which are composed of the new substance, caoutchouc and sulfur. We should expect these aggregates to be less active chemically, less plastic and less elastic if we may judge from what we know of hard rubber where the coefficient of vulcanization becomes sufficiently high. But how, it will be asked,

<sup>6</sup> The effect of over-milling and long cures will be dealt with in a later publication.

can we reconcile the statement that these aggregates are less elastic with the fact that cured rubber with a low coefficient of vulcanization is much more elastic than raw rubber. Therein lies the basis of the new plastic solid film theory applied to rubber that the author wishes to advance, which obtains not only in the case of cured pure gum but also in compounded stocks.

In this connection, one more assumption may be made which is entirely in accord with our knowledge of finely divided substances. When a small amount of sulfur is combined chemically with caoutchouc during vulcanization, it is probable that the caoutchouc in the lowest stages of polymerization is attacked first. This means that the matrix and not the large aggregates unites at first with the sulfur, by which process new aggregates are built up. If this is carried to the extreme, there should be little or no matrix left and the stress strain curves of hard rubber should approach those of metals. This is, of course, entirely in accord with the facts.

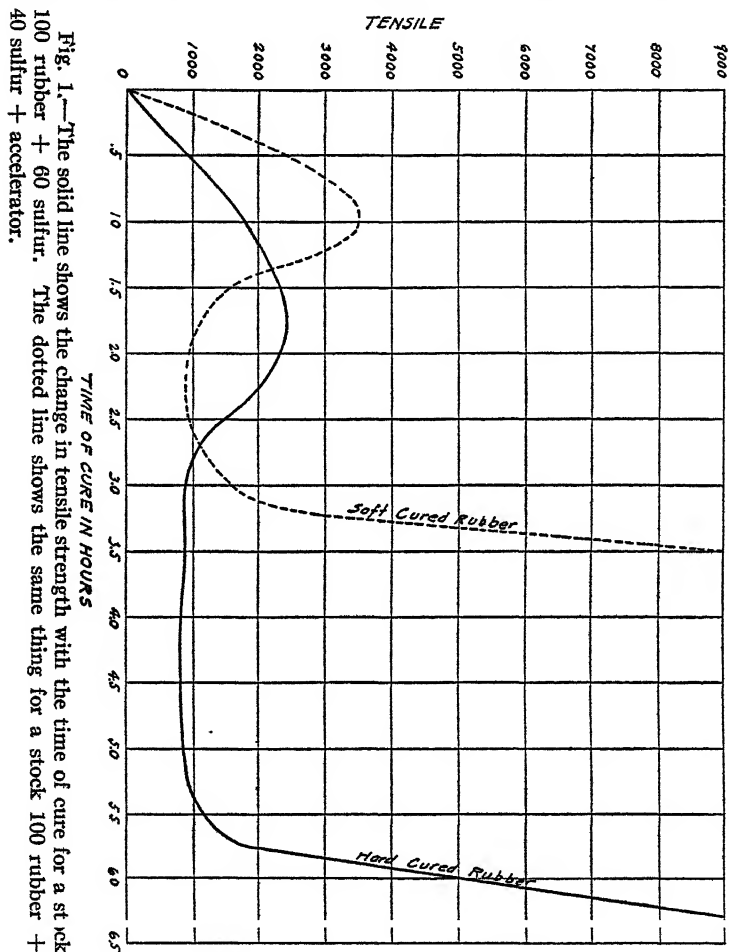
Another point must be kept clearly in mind, namely, that the vulcanization probably involves two opposing processes. The tendency of heat is to break down the large aggregates which are already present in the raw rubber, whereas sulfur combined with the matrix builds up aggregates of a new chemical substance. If we further assume that accelerators, natural and otherwise, are partially destroyed by the action of sulfur as the cure proceeds, we might easily explain the curious curves in Fig. 1, kindly given the author by W. W. Vogt of the Good-year Research Laboratories. The first portion of the curve would indicate that the sulfur is uniting with the matrix faster than the aggregates in the raw rubber are breaking down. There comes a period where the opposite is true and time must elapse before the building up process by the sulfur catches up with the depolymerizing effect of the high temperature.

#### PLASTIC FILM THEORY APPLIED TO RUBBER

R. E. Wilson<sup>7</sup> has shown that the formation of foam, soap bubbles for instance, is not due chiefly to surface tension effects, but rather to the plastic solid and elastic properties of thin films. If we apply this same theory to the case of rubber, it is not difficult to see that when the mass

<sup>7</sup> Paper read before the Colloid Symposium, Madison, Wis., June 12-15 (1923)

is stretched, the matrix between the larger aggregates will be thinned and we shall have films between the particles which act in a manner very similar to that of plastic films in foam. These films are much more resistant to distortion than the



thicker material from which they are made. For this reason, rubber should require a greater load to stretch it a unit length at higher than it does at lower elongations. The fundamental assumption of this theory is that in rubber, there exist some sort of aggregates in a surrounding matrix. It does not stipu-



late what the nature of the aggregates is, nor does it preclude the existence of more than one kind of aggregate. As will be seen later in this article, the author's theory will account for the shape of the stress-strain curves of cured rubber. It will also account for the reinforcing effect of compounding ingredients and will be further discussed under this heading.

#### STRESS-STRAIN CURVES OF RUBBER

There are very few stress-strain curves of raw rubber recorded in the literature. Those made on the Schopper's

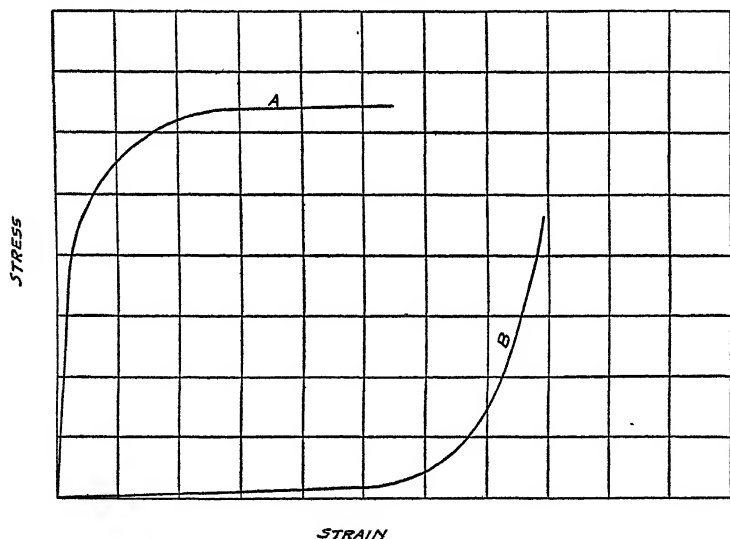


Fig. 2.—Curve A shows the shape of the stress-strain curve of metals; Curve B that of rubber.

machine<sup>8</sup> are almost straight lines showing great elongation and light loads. There is a most interesting field here for research, but before much headway can be made, it will be necessary to devise more suitable methods of testing than those now in use for vulcanized rubber. There seems little doubt but that a careful study of plasticity on raw rubber would throw considerable light on gel structure.

The stress-strain curves of most substances, metals for instance, plotted with stress as the ordinates and strain as the

<sup>8</sup> Whitby, "Plantation Rubber and the Testing of Rubber," page 284

abscissa run close to the perpendicular axis as in Fig. 2, Curve A. After the elastic limit is reached, the curve becomes convex with respect to the same axis. On the other hand, the stress-strain curves for cured rubber made from nearly pure gum stock, run close to the strain axis for low elongations and turn upward long before the point of rupture is reached as in Fig. 2, Curve B. Stated in words, this means that rubber is very easily stretched at first but becomes more obstinate as it is extended. It has been pointed out by several investigators<sup>9</sup> that the first effect of stress is to cause stretching and thinning of the matrix between the globular particles or aggregates and a consequent distortion of the latter. This distance between the particles would be increased in the direction of the extension but because of the shortening of the lateral diameters of the test piece, the globules or aggregates must approach closer and closer together. This would cause a compression of the plastic solid inside the elastic films and a greater load would be required to produce a given elongation.

The plastic film theory may be superimposed upon the explanations contained in the above paragraph. According to this, during the stretching process, plastic films of the matrix will be formed between the globules or aggregates. Further stretching of the mass would involve a movement of these films which are much more resistant than thicker layers of the same material. For this reason, it will require greater loads to produce given elongations as soon as these films become thin enough to have an appreciable effect. Hence the stress-strain curve as we have plotted it, must turn upward more rapidly the greater the elongation of the test piece.

#### JOULE EFFECT

When rubber is stretched small amounts while the temperature is low (1–5°C.) it becomes colder just as in the case of metals.<sup>10</sup> On the other hand, if it is stretched at room temperature, it becomes warmer and lastly, if the temperature is sufficiently high, rubber no longer gives out heat when stretched.

On the basis of the theories already outlined, rubber behaves like metals when the plasticity of the mass is very low and takes

<sup>9</sup> Lunn and others, *l. c.*

<sup>10</sup> Whitby, *l. c.*, p 453.

up heat when stretched. If the mass is at ordinary room temperature and then stretched, the matrix will give so that the particles are compressed. This distortion and compression of the particles should give out heat as is the case for any ordinary liquid or plastic solid. Finally, when the temperature is sufficiently high so that the plasticity of the mass is very great there is no longer any appreciable compression because the entire mass flows like any other plastic body.

#### SULFUR IN RAW AND CURED RUBBER

Sulfur may exist in rubber in several different physical and chemical forms.<sup>11</sup> It has been shown by several investigators that sulfur has a definite solubility in rubber and the solubility increases with the temperature at least between 35–98°C.<sup>12</sup> When raw rubber is mixed with sulfur and the temperature is raised, the sulfur will dissolve completely provided the solubility at that temperature is not exceeded. If the mass is now cooled under suitable conditions on the microscope slide, several interesting phenomena may occur depending upon the circumstances.

The sulfur and rubber form a supersaturated solution. If the supersaturation is sufficiently great, the sulfur will collect in small colloidal globules throughout the rubber mass. Sulfur in this state is very unstable for it is possible, either by seeding, or sometimes even pricking with a pin, to cause the sulfur to form a crystalline structure that has been called "dendritic." The crystallization takes place very rapidly and the long featherlike structure may be seen growing under a microscope. In no case has it been possible to form rhombic sulfur quickly under these conditions. The dendritic form invariably appearing first.

The dendritic form is in turn not stable for, in a short time, sometimes days, the dendritic form will change over into the rhombic. Sometimes, however, the sulfur forms rhombic crystals on the outside of the mass only, which phenomenon is called "blooming" in practice. Sulfur, which forms the

<sup>11</sup> Endres, paper read before the Rubber Section of the American Chemical Society, Sept. meeting, Pittsburgh (1922)

<sup>12</sup> Venable and Greene, *J. Ind. Eng. Chem.*, **14**, 319 (1922); Kelly and Ayers, paper read before the Rubber Division, Amer. Chem. Soc., April meeting, New Haven (1923)

bloom is, as far as we have any information at present, always in the rhombic form.

During the stage where the colloidal globules are changing into the dendritic form, there is invariably a clear space in the rubber between the globules and the dendritic crystals. It would seem as if the globules dissolved in the rubber and that the crystals were formed from the dissolved sulfur. This would indicate that the solubility of the colloidal sulfur is considerably greater than that of the rhombic crystals.

#### COMPOUNDING MATERIALS

Leaving sulfur out of consideration, the substances which are usually added to rubber for technical purposes may be divided into three classes:

1. Those such as zinc oxide and gas black which impart desirable qualities to the rubber mass (these will be dealt with later).

2. Those such as mineral rubber, hardwood, pitch, vegetable oils, etc., which are added to facilitate manipulation of the rubber through the factory. Many of these also lower the cost and therefore act as Class 3.

3. Substances called "fillers" which have little effect upon the rubber, except to dilute it and lower the cost.

In dealing with the properties of compounding materials, carbon black will be chosen because its effect on the rubber is more pronounced than any other substance known. Zinc oxide is, of course, of very great importance but what we have to say can be well illustrated with carbon black.

Carbon black is made today chiefly from natural gas. Several processes are employed in technical practice but it is not the purpose of this article to deal with these but rather with the character of the carbon black itself. Carbon black when dispersed in a suitable liquid medium, viewed in the ultra-microscope or in dark ground illumination, reveals a considerable portion of particles that are in rapid Brownian movement. On the other hand, there is a very great variety in the diameter of the various particles present. Some are large enough to be seen quite readily with oil immersion and magnification of less than 1000. That is to say, the particle size in the different varieties of a technical carbon black generally differs

very greatly. Whether the larger particles are real individuals or whether they are merely agglomerations of smaller particles is not known definitely. It is probable however, that both large entities and agglomerations are present. The average diameter of the particles differs from  $0.1\text{--}0.2\mu$  up to about  $0.6\mu$ , for different samples of technical carbon black procurable on the market.

It is generally conceded by rubber chemists that the size of the particles is an extremely important feature of compounding ingredients and that the smaller the particles within certain limits, the greater the effect of the material on the rubber. Some recent investigations under the direction of the writer have indicated that another very important factor is involved in this connection. It has been shown beyond reasonable doubt, that the carbon black which has particles of the smallest average diameter when dispersed in an aqueous medium is not necessarily the most effective for use in rubber. It seems

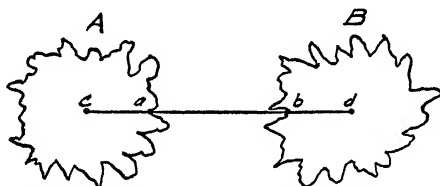


Fig. 3.—A diagrammatical sketch of carbon particles with irregular surface.

much more probable that the carbon black which will disperse best in rubber is to be preferred. In other words, we have to deal here with the average diameter of the carbon particles including agglomerations in rubber rather than the average diameter as determined when the carbon black is dispersed in other media. If the point of view of the rubber chemist is correct, then that carbon which exists in the finest state of subdivision in rubber is the most valuable.

Another property of carbon black is doubtless of fundamental importance, not only for use in rubber but also in inks, enamels, paints, etc. This property has to do with the character of the surface of the particles. It seems probable that this surface of the most valuable types of carbon black may resemble a burr rather than that of a marble. In other words, the particles

are very deeply serrated so that the actual surface is very much larger than the diameter measurements would indicate. On the other hand, on some kinds of carbon, the surface of the particles is probably much smoother, such, for instance, as can be observed on a piece of graphite. It should be remembered that the measurements of the diameter will be those represented by the greatest distance across the particles so that in case a particle is somewhat star shaped as in Fig. 3, the diameter would bear very little relation to the surface. In other words, in compounding materials, we have to do with free surface and perhaps surface energy rather than with the diameter of the particles.

#### PARTICLE SIZE

It would seem altogether probable that there is a limit to the fineness to which the particles of any one substance may be reduced in order to obtain the maximum compounding effect, such, for instance, as reinforcing. For, we know of no substance of low molecular weight such as sodium chloride in a state of molecular subdivision, that will reinforce rubber. Stated in other words, this means that any substance which will mix with rubber in such a way as to follow the laws of solubility will not reinforce it. On the other hand, it is well established that, within the limits of the ordinary microscope, the reinforcing property of a given pigment is an inverse function of the size of the particles.

If we attempt to plot the reinforcing power against the average size of the particles, one end of the curve must go through or near the origin.<sup>13</sup>

The reinforcing curve must therefore go through a maximum between these limits and have some such shape as Curve A, Fig. 4. The dotted portion is employed to indicate that there are no recorded observations in this region.

It will be noted that this curve is very similar to that drawn by Alexander which he has named the curve of "optimum colloidity."<sup>14</sup>

As pointed out by Alexander, the fundamental principle underlying optimum colloidity is the relation between "kinetic

<sup>13</sup> The origin has been taken arbitrarily at a diameter of  $1\mu$ , whereas the other reaches the abscissa somewhere about the order of magnitude  $1-10\mu$

<sup>14</sup> Paper presented before the Colloid Symposium, Madison, Wis., June (1923)

activity," amount of surface and the size of the particles considering a unit weight of substance. The kinetic activity of the particles increases more rapidly with decreasing diameter than the total surface increases. Alexander plotted these two values on the same plot, curves C and B respectively, against the size and pointed out that the two curves must cross as in Fig. 4.

It is not difficult to see from the above considerations that however desirable it may be from the compounder's standpoint to decrease the size of the particles and therefore increase the total amount of surface, a limit will be reached beyond which we cannot go, because the kinetic activity of the particles becomes

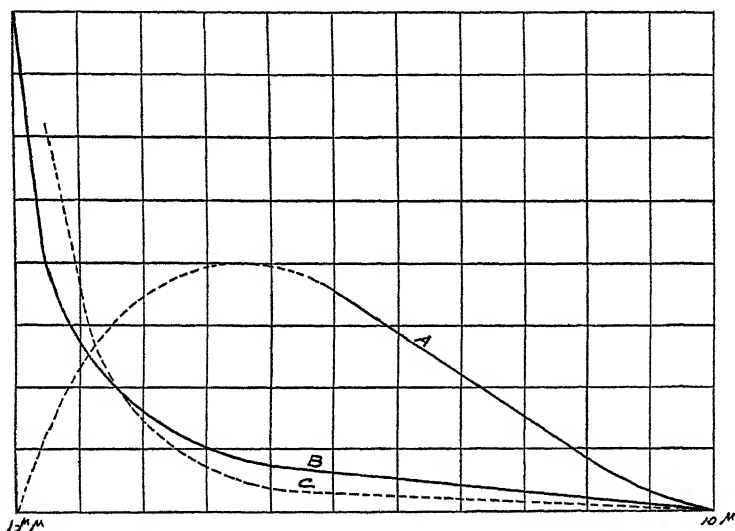


Fig. 4.—Curve A represents the reinforcing value of a given pigment; Curve B the surface for a unit weight of substance; and Curve C the kinetic activity of the particles, plotted against the diameter.

so great that the mass will be rendered more plastic instead of being reinforced. Just at what diameters the reinforcing maximum will occur should prove an interesting and valuable field for research.

Another point will be of interest to those working with compounding materials. By what means could we increase the total surface and not at the same time raise the kinetic activity of the particles to undue proportions? While there are no very definite experimental data to prove the point, it is the opinion

of the author that the question has been answered in a practical way by the manufacturers of compounding materials such as carbon black and zinc oxide. The methods here employed are those of condensation and not that of grinding. If particles are grown from a material in a finer state of subdivision, such as the formation of carbon black from natural gas, it should be possible to obtain an irregular surface like that of a burr instead of a plain surface like that of a highly polished metal. Therefore, the total amount of surface on a unit weight of substance would be considerably greater than we should expect from a knowledge

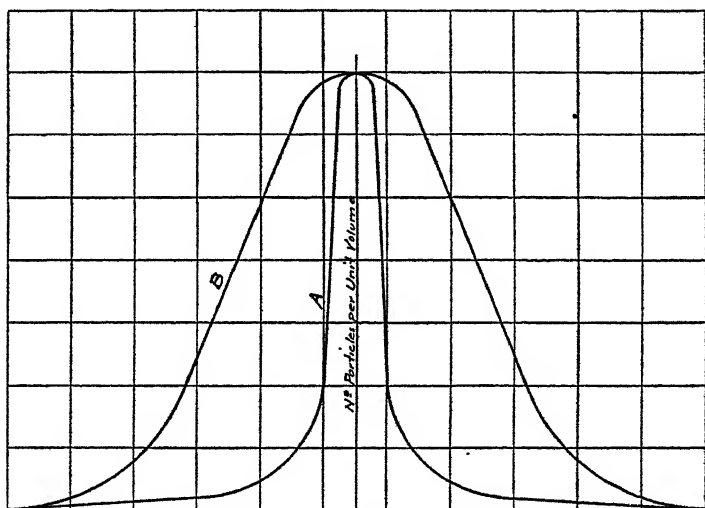


Fig. 5.—Curve A represents the distribution of the particles about the mean diameter of an ideal compounding material; Curve B shows the same thing for concrete or a paint film.

of the average diameters of the particles and the kinetic activity of the particles correspondingly less. This is doubtless true in the case of carbon black.

Grinding, on the other hand, can give only an irregularly shaped particle, the surfaces of which more nearly resemble planes. We should expect, therefore, for the same sized particles, to obtain a greater reinforcing power for the use of particles formed from condensation than from those obtained by grinding. It will be interesting to see if this can be proven or disproven by future investigation.



Another fact of importance which has not been sufficiently investigated is the distribution about the mean diameter of the particles. In the mixing of concrete use is made of the principle of minimum voids. For this reason, the particles should differ in size and the distribution occurring around the mean might be represented by Curve B, Fig. 5. On the other hand, if the main consideration in compounding materials is amount of surface within the limits outlined below, and if the problem of minimum void has little to do with the case, then the distribution curve would have the general character represented by Curve A, Fig. 5. It seems extremely improbable that the principle of minimum voids is applicable to the use of compounding materials in rubber for the volume occupied by the compounding material is usually much less than that occupied by the rubber. This would indicate that the rubber takes care of the voids and that compounding material has little to do with this principle.

#### EFFECT OF COMPOUNDING MATERIALS

Compounding materials such as carbon black produce a pronounced change in properties of rubber. Even the uncured mass is rendered much stiffer by the incorporation of carbon black. In the case of cured rubber, the load at 300% elongation or the stiffness of the mass, is very greatly increased whereas the total elongation at break is materially reduced. Moreover, the tensile strength at break is much greater when the proper amounts of carbon black have been incorporated. The wearing quality of rubber containing carbon black is unsurpassed by any other known combination, although some other compounding ingredients, such as zinc oxide, greatly improve the wearing qualities of pure rubber. Another effect of carbon black is to increase the resistance of the mass to tearing. The resistance to tear and the wearing properties are, of course, of extreme importance in technical practice. The very pronounced change in properties of rubber, due to the presence of carbon black, is well illustrated by the stress-strain curves in Fig. 6. Especially noticeable, is the increase in the load at 300. This property is of very great importance in the case of pneumatic tire treads and solid rubber tires.

All compounding materials impart to the rubber a property

which is known in technical practice as "grain." This grain is not to be confused with the grain which results in pure rubber by calendering or sheeting out on the mill. The latter is done away with to a large extent during the cure while the grain, due to compounding materials, is not affected to any appreciable extent by the heat treatment. It may, however, be obliterated

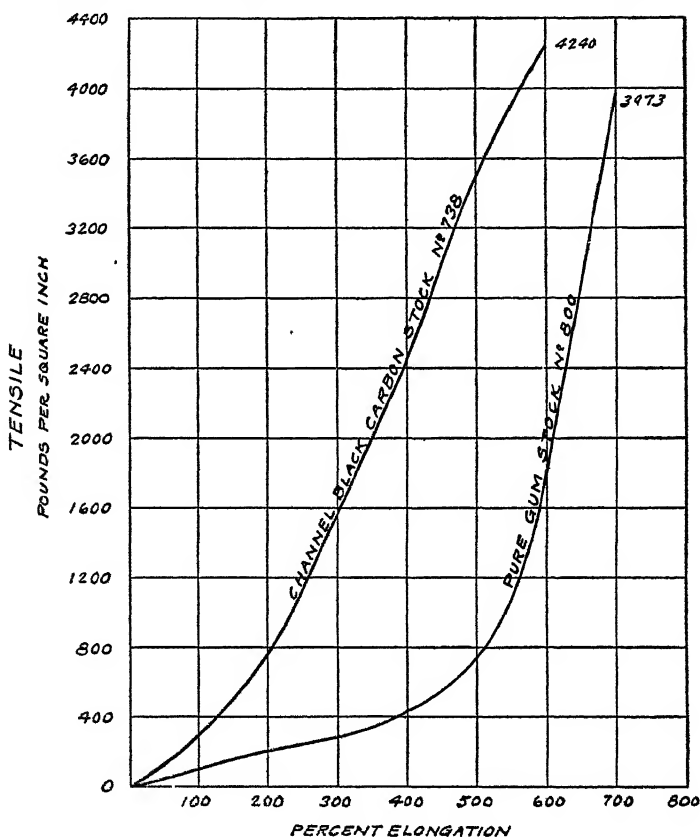


Fig. 6.

in part by the mechanical manipulation of the stock, such as squeezing in the mold. This has been well demonstrated by Wiegand and Braendle.<sup>15</sup>

Referring again to the grain as imparted by compounding

<sup>15</sup> *J. Ind. Eng. Chem.*, **15**, 259 (1923)

materials, attention is called to an article recently presented by Vogt and Evans.<sup>16</sup> In this article, a good case is made for the effect of the shape of the particles. If materials which have flat flakelike particles or acicular crystals are incorporated into the rubber, the modulus in the direction perpendicular to the rolls is materially less than the modulus in either of the other directions. This is explained on the assumption that as the rubber is stretched, it is able to flow freely between the flat surfaces of the crystals, due to the fact that spaces between the latter are relatively large. The crystals take up a position with

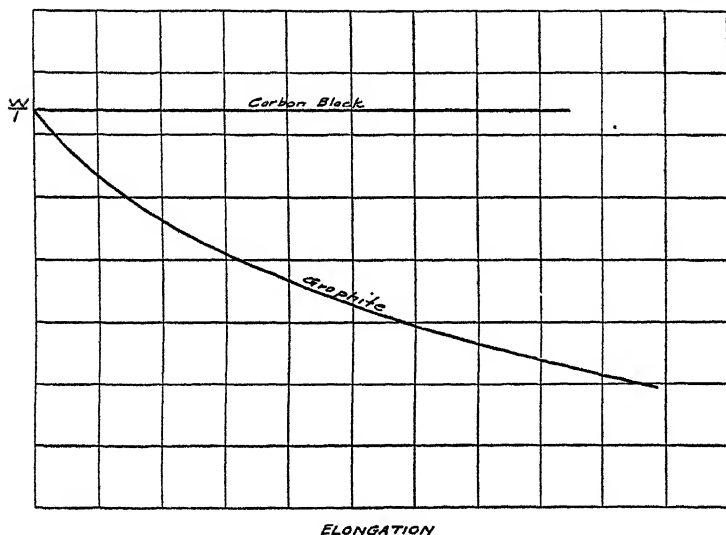


Fig. 7.

the flat side presented to the roll during the milling and will obviously over-lap in the other two directions. When the rubber is stretched in the direction perpendicular to the roll, the portions between the flat crystal consisting of practically pure rubber should stretch quite readily and the elongation at break should be considerably greater than it is in either of the other two directions. This is found to be the case.

This same phenomenon is very well revealed by the last named authors' determination of Poisson's ratio in the two directions

<sup>16</sup> Paper presented before the Rubber Division, Am. Chem. Soc., New Haven meeting, April (1923)

normal to the longest diameter. Perhaps their method of treating this, as shown in Fig. 7, is more easily comprehended. Here it will be seen that if the width of the test piece, divided by the thickness is plotted as the ordinate and the elongation as the abscissa the curve for carbon black is practically a straight line and parallel to the abscissa. This means that as the rubber is stretched, the change in diameter is the same in at least two directions, which would indicate that the rubber mass is isotropic. It will be readily seen on the other hand, from the curve for graphite, that the rubber is anisotropic.

#### CAUSE OF INCREASED TENSILE AND DECREASED ELONGATION

The most reasonable theory offered up to the present to explain these phenomena is in harmony with our knowledge of colloidal substances. It is believed that the rubber is adsorbed on the surface of the carbon particles and that adsorption (so familiar to colloid chemists) is the real cause of the effect of carbon black in rubber. It is clear that if rubber containing compounding ingredients is stretched and if the rubber is adsorbed on the surface of the particles, the portion that is on the immediate surface ought to have less extensibility than the original rubber. Moreover, granting the rubber between the particles were to have the same extensibility that it had before incorporation of the compounding ingredient, it is clear that the total elongation of the mass would be much less than if pure rubber only were present because a considerable portion of the distance between the grips is taken up by the particles of the compounding material. This can be illustrated by Fig. 3. If A and B are two particles of compounding material separated by comparatively pure rubber, A-B, then the total stretch from point C to D cannot be so great because in that case the pure rubber between the particles, A-B, would have to stretch more before rupture than it would if the entire substance from C to D were pure rubber.

As for the increase in tensile, we have here to deal with two phenomena which are diametrically opposed to each other. It is quite easily imagined that if the rubber is adsorbed on the surface of the particles, the properties of the former should be very materially modified, that is to say, the tensile which is necessary to tear it apart might be very much greater because of

the influence of the force of adsorption. On the other hand, it should be remembered that in order to distribute carbon black, or any other compounding material in rubber, it is necessary to mill or mix the rubber for a considerable period with the compounding ingredient. This, of course, tends to degrade the quality of the rubber but the carbon black will undoubtedly adsorb the matrix and thus in a measure offset the degradation.

According to the plastic solid film theory, the films between the solid particles of carbon black are much more resistant to distortion than the matrix would be were no compounding present. This explains at once why the mass is stiffer and why the curves for carbon black stocks partake very nearly of the nature of straight lines. Even for low elongations, these films are thin enough to become operative, whereas in the case of pure gum stocks, the stretching process must proceed a considerable distance before the matrix is thinned sufficiently to form effective films. Finally, these films are very strong hence we should expect the ultimate tensile of carbon black stocks to be high, which is, of course, in accordance with the facts.

Another interesting phase connected with high tensiles deserves mention. Whitby<sup>17</sup> has reported a tensile of 4700 pounds per square inch, original cross section for nearly pure gum stocks. The author has obtained 4000 pounds using a different accelerator. In these cases, the time of milling and curing was short which means that the aggregates or complexes originally present in the rubber were not destroyed by milling or by heat. More films would be formed therefore when the rubber was stretched and the ultimate tensile should be high according to the theory. It is a safe prediction however, that if carbon black could be incorporated into the pure gum without subjecting the mass to a long milling process and if the curing time could be very short, the tensiles would be still higher.

In keeping with the film theory, the distinction between mere fillers, such as whiting, and those substances which reinforce rubber to an appreciable degree, lies in the hypothesis that the latter adsorb rubber strongly, whereas the former form a very weak union with it. If the bond is not sufficiently strong there can be no plastic solid films formed and therefore little or no stiffening action.

<sup>17</sup> Paper read before the Rubber Division, Am. Chem. Soc., New Haven meeting, April (1923)

## SOFTENERS

North and Ault have proposed a theory to explain the increased plasticity of rubber due to the incorporation of certain substances such as oils, mineral rubber, resins, etc. They believe that the aggregates in the rubber are broken down to some extent by the softener. Judging from their data, this seems to be true when the mass is heated but it is difficult to see why these softeners are so effective while the rubber is raw and temperature relatively low as it is during the milling. It seems much more probable that the softener increases the amount of matrix between the particles and therefore lubricates them, so to speak. While the mass is being vulcanized, the softener may depolymerize the rubber but it must not be forgotten that many such substances unite with sulfur so that the resulting action will be the sum of two opposing reactions. This may account for the fact that many softeners affect the raw rubber to a much greater degree than they do the cured mass.

## DISCUSSION ON E. B. SPEAR'S PAPER

COLLOIDAL PROPERTIES OF RUBBER AND  
COMPOUND INGREDIENTS

E. F. BURTON: I would like to ask Dr. Spear if they have any colloidal material that they can put into rubber that will bring it between the maximum and the minimum side.

E. B. SPEAR: We do not know yet. I have tried a great many different samples of colloidal materials, zinc oxide, barium sulphate, etc., but you will see the difficulty at once. We do not know the relation between the real surface area of the particles and their diameter, if the surface is at all irregular. Now if you grind these particles, you are going to have a much smoother surface, and as long as we do not want to get that result, the better method is to grow the particles and not grind the material at all.

E. F. BURTON: Have you any evidence that the intensity of the Brownian movement has a shattering effect?

E. B. SPEAR: No.

W. A. GIBBONS: I was interested in Dr. Spear's speculation as to what happens when the latex is dried out. I have worked with latex a good deal, but what happens, as far as I was able

to see, is this, when you either dry latex or coagulate it, the globules come together, and if you don't do anything else to them they stay in the sheet, but if you melt that rubber you will not be able to identify the original particles. It is an interesting speculation that we have no evidence for at the present time. I never could quite see the stand taken by Pratt. It seems perfectly absurd to me that if you take rubber and dissolve it, and it gives you a very thin mass of rubber, and then by a purely mechanical process subdivide that solution into very fine drops—I see absolutely no reason for assuming that those drops consist of simply the original latex particles. With reference to the question of fillers, I think the points brought out by Dr. Spear are very interesting. There was a paper some time ago that dealt with some previous work done in Canada, indicating that there is a specific action arising from the condition of the surface, aside from the question of size. It seems to me that any curve such as that drawn by Mr. Alexander would not be applicable, as it stands, to the question of rubber fillers, unless you also take into account the question of specific surface. I do not think anybody has brought out any clear explanation as to why some surfaces act and others do not. If you take some fillers and stretch them you will find that the rubber filler surface is continuous. In other cases, however, the rubber actually pulls away from the filler. Of course the shape of that would have a lot to do with it. That is just ordinary mechanics. Why two surfaces of the same identical shape and size act that way I do not know.

E. B. SPEAR: It seems to me that is merely a case of selective action. I would not expect two rubbers to act the same way. It must be confessed that we have comparatively little experimental data as yet regarding many things, and that is so in the case of rubber. The facts are that with a great many substances—for instance graphite, the volume increases when the rubber is stretched. If I take gas black stock and do the same thing I cannot get any volume increase unless the particles are present in huge conglomerations.

With regard to the shape of the particles, I wish I could take up Mr. Vogt's papers. I have discussed that matter with Mr. Vogt many times and have gotten some very valuable information out of it.

The astonishing fact is that if we stretch a piece of rubber which contains flat particles of compounding material, according to the hypothesis of Mr. Vogt, the percentage decrease in width of the test piece is quite different from that of the thickness. We have, therefore, different properties in the three directions at right angles to each other. I do not want to give you the mathematics of that because we haven't time, but it is a very interesting subject.

R. THIESSEN: There are two points that I desire to speak about, and they concern the conglomeration of particles. I have looked at a good many carbon blacks in my time. Every carbon black and every substance that is composed of carbon at all has one and the same unit particle. I mean the primary particle. It is an oblong particle as far as I can tell anything about it. I believe the carbon particle is an oval. The very best theoretical carbon black would be that carbon black in which the whole mass is dispersed in unit particles. But I have never yet seen any carbon that. . . .

J. ALEXANDER (interrupting): What kind of an instrument was that looked at with?

R. THIESSEN: With the best Zeiss apparatus available.

J. ALEXANDER: Was that an ordinary microscope?

R. THIESSEN: No, an ultramicroscope.

J. ALEXANDER: You say they have an indefinite shape. . . .

R. THIESSEN: But it doesn't make any difference where I see it.

J. ALEXANDER: If these particles had a definitely visible shape, they must have been considerably larger than colloidal dimensions.

R. THIESSEN: You don't see the colloidal dimensions.

J. ALEXANDER: You don't get what I mean. If these particles had a definitely visible shape, they must have been of dimensions large enough to reflect wave lengths in the visible range.

R. THIESSEN: In the very best carbon black we have three per cent. of dispersed particles. The rest of the carbon black consists of a number of particles put together and you can see the particles and you can see the spaces between them. Now the very best carbon black has a lot of these particles with a lot of small secondary particles. Now, I never saw this shape here



(indicating), but you have this other particle (indicating) and it is made up of unit particles, with the spaces in between, and they are in a way flexible, except in those carbon blacks where you have principally solids. Upon that of course depends the adsorbent capacity of the carbon.

Now, another remark I want to make is on the original colloid particle. I do not know anything about rubber latex, but I have seen a lot of other substances, wood for example, or coal. A piece of coal can be peptized and one sees (in the ultramicroscope) the particles in that fine piece of coal, and they are of the same appearance and have the same characteristics in the solid coal as they have in the colloidal solution. In the case of wood you can see the colloidal particle, or if you peptize it the very same particle that you can see under the ultramicroscope just flies off. Now I take this same colloidal solution and precipitate it with sulphuric acid, and take the very smallest amount of sulphuric acid, and these particles all come together again. Now that sort of study that I am forced into every once in a while makes me believe that ultra particles exist in certain substances. In those solids, as far as my observation went, I could see those ultra particles, and when I dissolve them I can see those same particles present.

W. G. KELLY: There are a couple of points I would like to ask Dr. Spear about. In the first place regarding this contraction of rubber at milling, after that rubber has been milled a short time it will change, and if you mill it for half an hour it will not change.

E. B. SPEAR: I differ with you. I have found in some experiments that the rubber changed somewhat after milling one and one-half hours, but of course not to so great an extent. We would not expect it to change as much if the milling has destroyed the original particles.

W. G. KELLY: Regarding the sizes, just what are they?

E. B. SPEAR: It is about the average size of the process that you are using every day, I do not think it is the maximum size at all that we are discussing here.

The effect of milling depends upon a number of factors such as, the time, temperature, differential between the rolls, the thickness of the sheet, speed of the mill, diameter of the rolls, plasticity of the compound, and possibly others.

W. G. KELLY: I don't follow you, Dr. Spear. Those particles are practically all broken up.

E. B. SPEAR: According to some of the work we know that some of them are.

H. S. TAYLOR: I just want to say that this is obviously another case where we ought to get together and work with the same instruments.

E. B. SPEAR: The trouble in this case, Dr. Taylor, is that Dr. Kelly and I have worked together in the same laboratory for three years!

# THE DISPERSITY OF THE SILVER HALIDES IN RELATION TO THEIR PHOTOGRAPHIC PROPERTIES

BY S. E. SHEPPARD

## INTRODUCTION

The pioneers of the photographic process<sup>1</sup> were well aware that by the variations of vehicle, of temperature, of salts and other substances present, they obtained different appearing and different behaving forms of a given silver halide—AgCl, AgBr [AgI].<sup>2</sup> The nature and ground of these differences were, however, only vaguely assigned to "molecular modifications," as were also characterized by Stas<sup>3</sup> the different types of precipitates he obtained in his investigations on the atomic weight of silver.

Later investigation has shown that all these "modifications" consist of one form only of the silver halide in different degrees of dispersity, different stages of aggregation—at the same time contaminated with different amounts of adsorbed electrolytes. All modifications of the silver halides are crystalline, including the amorphous precipitates and colloid hydrosols, in which no crystalline form can be observed with high power microscopes. This has been shown by X-ray spectroscopy.<sup>4</sup> The crystals belong to the following systems and classes.<sup>5</sup>

	AgCl	AgBr	AgI	
System	Regular	Regular	Regular	Hexagonal
Class		Dyakisdo-dekahedral	Dyakisdo-dekahedral	Tetrahedral lattice, hexagonal arrangement
Lattice	Simple cubic	Simple cubic	Simple cubic (metastable below 147°C.)	(stable form below 147°)

Now as to the occurrence of the silver halides in regular

<sup>1</sup> Cf. for example, W. deW. Abney, "Photography with Emulsions"

<sup>2</sup> Silver iodide only used in small amounts with silver bromide

<sup>3</sup> J. S. Stas, *Ann. chim. phys.*, **3**, 145 (1874); cf. J. M. Eder, *Handb.*, Vol. III, 5th Ed. (1903)

<sup>4</sup> R. Wilsey, *Phil. Mag.*, **42**, 262 (1921)

<sup>5</sup> A. P. H. Trivelli and S. E. Sheppard, "The Silver Bromide Grain of Photographic Emulsions," p. 129

photographic emulsions, it should be noted first that the sensitive silver halide preparations may be divided into two main classes.

1. Silver halide formed in presence of excess soluble silver salt.  
This class includes: wet collodion, collodion emulsion, most printing out emulsions.
2. Silver halide formed in presence of excess soluble halide.  
This class includes both positive and negative emulsions for development.

These two classes may be regarded as derived from two different types of silver halide hydrosols, *viz.*, those in which the hydrosol particles are stabilized by adsorption of silver ions and those in which they are stabilized by halide ions.<sup>6</sup> This adsorption is associated with peptization<sup>7</sup> and thereby actually with the solubility of the halide in the component in excess. This increases for the series  $\text{AgCl} \rightarrow \text{AgBr} \rightarrow \text{AgI}$  in the order given.

Two types of reduction of dispersity come into play in the formation of actual emulsions. These are (I) flocculation (coagulation), (II) recrystallization. The first of these consists in the coagulation of hydrosol particles to a hydrogel, by neutralization of the stabilizing charge. The hydrosols of the silver halides, prepared in absence of protective colloids, (which is only possible at very considerable dilutions) are relatively easily coagulated by electrolytes. This is particularly the case where a sol of  $\text{AgX}$  stabilized with excess  $\text{Ag}^+$  ions is precipitated by addition of a salt of the anion X, and conversely. On the other hand, when formed in the presence of protective colloids, *e. g.*, gelatin, casein, the silver halide hydrosols are relatively very stable as regards electrolytes. They are, however, easily flocculated by solvents for silver halides<sup>8</sup> and in this case it is certain that the process (II) of recrystallization is largely overlapping or indeed superseding the process (I).

The influence of such solvents as ammonia, alkaline bromides, thiocyanates, upon the flocculation of silver halide hydrosols in gelatin has been studied qualitatively by Lüppo-Cramer.<sup>8</sup>

A suitable "grainless" emulsion of the Lippmann type may

<sup>6</sup> A. Lottermoser, *J. prakt. Chem.*, N. S., **56**, 241 (1897); **71**, 296 (1905); **73**, 374 (1906)

<sup>7</sup> W. D. Bancroft, *J. Franklin. Inst.*, **185**, 376 (1918)

<sup>8</sup> Phot. Probl., p. 9

be prepared by mixing together at 35–40°C. equal volumes, *e. g.*, 500 cc. each, of 10 per cent. gelatin solutions, one containing 1.5 g. KBr per 100 cc., the other 2 g.  $\text{AgNO}_3$  per 100 cc. The addition of electrolytes, which do not combine with silver halide, to this has no appreciable effect, even on warming, but small quantities of  $\text{NH}_4\text{OH}$ , KBr,  $\text{Na}_2\text{SO}_3$ , KCNS, produce upon warming a rapid increase in opacity and very soon a definite granulation. Lüppo-Cramer points out that it appears difficult to attribute this ripening entirely to the recrystallization (Ostwald ripening) process noted immediately, since it is also effected by certain substances which can hardly be considered as dissolving or combining with silver bromide, *viz.*,  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_4$  (slight),  $\text{NaNO}_2$ ,  $\text{NaHSO}_3$ ,  $\text{HCl}$ —the last, having a very strong action may be considered as reacting, certainly with  $\text{AgCl}$ , however.

Very little work of a quantitative character has been carried out on the flocculation aspect of ripening in these very fine grain emulsions used for development, generally on paper. These emulsions run through the gamut of  $\text{AgCl} \rightarrow \text{AgCl} : \text{AgBr} \rightarrow \text{AgBr}$ , *i. e.*, from pure silver chloride through chlorobromide to pure silver bromide emulsions, (bromide papers). The grains of these D. O. P. emulsions, without being entirely ultramicroscopic, seldom exceed  $.3\mu$  in diameter; they probably have, even at this small size, a gel structure, partly consequent on flocculation phenomena as described above, and which is of great importance as determining the tone and tonality of the developed prints. It must be noticed, however, that the quantitative investigation of the dispersity factor here is beset with difficulties. It is difficult, if not impossible, to apply the sedimentation technique which can be used with gelatin free suspensions and hydrosols—and any method of study which involves removal of the gelatin will be liable to change the secondary and ternary particles which it is desired to investigate. The process of reduction to silver, in development, does not throw any necessary backward light upon these points, since the developers used contain, in sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) a solvent for the silver halide, and therefore the relation between silver halide particle and developed silver particle is much more seriously disturbed than in the case of the negative emulsions to be discussed shortly.



a range, 1 to 180,000 or more, should depend upon a change of dimensions of the order:

Linear.....	1 to 10
Area.....	1 to 100
Volume....	1 to 1000 (actually less, because the larger grains are flat tablets)

As a matter of fact, it has been recognized that coarse grain is not sufficient for high speed. Thus Trivelli and Sheppard point out:<sup>11</sup> "In practice, indeed, it often seems that the coarse-grained emulsions are more sensitive than the fine-grained. But that this is not always the case is shown by the following:

An experimental emulsion was prepared, the grains of which measured up to  $8\mu$  in diameter, and which had an H. and D. speed of only 38. In comparison with this emulsion, a 'Royal Standard Lightning Plate' from Kodak Limited was tested, the grains of which averaged up to  $2.8\mu$  in diameter, and of which the H. and D. speed was 728. Thus it appears that emulsions containing grains of approximately one-third the linear dimensions are more than nineteen times as sensitive." Comparable statements have been made by F. F. Renwick<sup>12</sup> and others. This insufficiency of grain-size for photographic sensitivity has now been shown quantitatively, in a very convincing manner, by the production of emulsions by the same formula, with statistically identical grain-characteristics (dispersity and distribution) but with totally different photographic characteristics, (v. infra).

Before the details of this, and the further discussion of the necessity, or otherwise, of coarse grain for high sensitivity, we must consider more closely the actual dispersity and its range in emulsions, and the specification of their photographic characteristics.

#### DISTRIBUTION OF GRAIN-SIZES

The fact that the grains in any emulsion are not uniform in size was evident from the early microscopic examinations.<sup>13</sup> Attention to the possible influence different distributions might

<sup>11</sup> "The Silver Bromide Grain of Photographic Emulsions," p. 104

<sup>12</sup> *Phot. J.*, **45**, 333 (1921)

<sup>13</sup> Cf. V. Bellach, "Die Struktur d. photographischen Negativen" (Knapp Halle, 1903; S. E. Sheppard and C. E. K. Mees, "Investigations on the Theory of the Photographic Process," 1907

have on the photographic characteristics was first drawn by C. E. K. Mees.<sup>14</sup> Somewhat later, R. E. Slade and G. I. Higson<sup>15</sup> suggested that for the attainment of very high contrast, as desired in "process" or photomechanical plates, a very uniform grain is necessary. But the first quantitative examination of the relation of grain size to sensitivity in one and the same emulsion was made by The Svedberg.<sup>16</sup> Not only this, but Svedberg furnished photographic chemistry with a new and valuable method of grain analysis. After exposing a layer of grains one-grain deep to a series of exposures, and developing, he removed the developed silver grains, and counted and measured the unchanged grains. By comparison with the statistics of the untreated layers, the number of grains of a given size-class (size being taken as projective area) affected by a given exposure could be determined, hence also the relative proportions of grains in each class affected, *i. e.*, made developable, by the same exposure. We shall return to this shortly. At this time the author and his collaborators, E. P. Wightman and A. P. H. Trivelli, were developing methods for the statistical analysis of grain sizes in emulsions. These are described elsewhere<sup>17</sup> and it is only necessary to state that a layer of diluted emulsion one grain deep is coated on special plate glass, care being taken that the grains are uniformly distributed and nearly all in one plane. Photomicrographs at 2000 to 2500 diameters were made, with high resolution systems. These were further enlarged by projection printing, so that a magnification of 5000 to 10,000 was obtained. The areas of grains were measured and classified, and size-frequency curves plotted.

Generally for photographic purposes it is desirable to use projective area as the parameter for grain-size. By multiplication of any projective area size-class by the number of grains of that class per unit area of the plate, the "covering power" of grains of that size is easily obtained, *i. e.*, their integral light stopping power.

In Figs. 1 and 2 are shown typical size-frequency curves of different emulsions.

It was found that either of the two following types of equations

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<sup>14</sup> *J. Franklin. Inst.*, **179**, 141 (1915)

<sup>15</sup> *Phot. J.*, **59**, 260 (1919)

<sup>16</sup> *Z. wiss. Photo.*, **20**, 36 (1920)

<sup>17</sup> *J. Phys. Chem.*, **25**, 181 (1921); **25**, 561 (1921); **27**, 1 (1923)



would fit fairly well the data classified on a uniform diameter basis

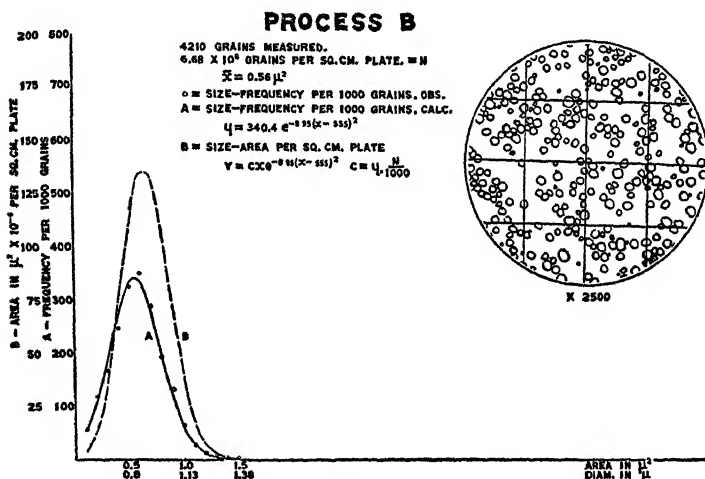


Fig. 1.

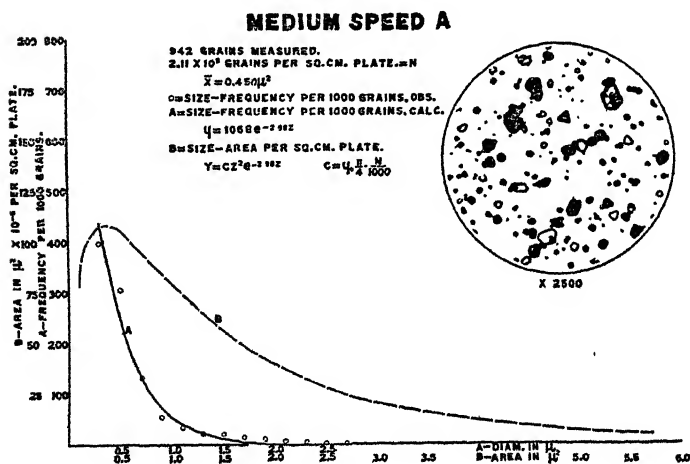


Fig. 2.

$$y = y_0 e^{-kx} \quad (1)$$

$$y = y_0 e^{-k(x-\alpha)^2} \quad (2)$$

Where  $y$  = frequency (per 1000 grains),  $y_0$  the intersection of

the curve with the  $y$ -axis, for (1) and the maximum ordinate for (2) while  $k$  is the "precision" or "deviation" constant,  $z$  the class-size in diameter,  $\alpha$  a constant indicating the position of the maximum ordinate on the axis of  $z$ .

Equations of the same form were found to be applicable to the uniform area classification

$$y = y_0 e^{-kx} \quad (3)$$

$$y = y_0 e^{-k(x-\alpha)^2} \quad (4)$$

where  $x$  equals class-size in area.

The exponential type probably represent a portion of a curve of the second type, in which the first part could not be measured because of the smallness of the grains. We have indeed a series in which transition from the exponential to the Gaussian type is clearly shown.

The origin of the given distribution appears likely to lie in the following conditions. The formation of the emulsion is a process of group crystallization. The starting point here appears to be the preliminary distribution of ionic and molecular velocities in the reacting solutions. This will be represented by Maxwell's "error function" in some form. Thus the number of ions having velocities between the limits  $v$  and  $v + dv$  will be

$$dn = CN e^{-3v^2 \frac{2}{v^2}} v^2 dv \quad (5)$$

where  $N$  is the total number in the system, *e. g.*, per unit volume,  $\bar{v}$  is the root-mean-square velocity, and  $C$  is a constant.

Further, the velocities (Brownian movement) of the first colloidal particles of insoluble precipitate formed will be similarly distributed, both as regards translational and rotational movements, and stirring (agitation) as a first approximation may be regarded as only affecting the constant,  $C$ .

It appears probable, from consideration of the effect of stirring and other factors that collisions of particles, including smaller ones with larger ones of lower velocity, play a considerable part in the determination of the initially rapidly changing distribution. That is, collisions of particles with particles as well as of ions with particles contribute to the initial crystal growth. These collisions may be either elastic or inelastic, in the latter case adhesion and growth being effected. Von Weimarn supposed

that as the concentration of the reacting ions is increased the dispersity goes through a minimum. This was found to hold apparently for precipitated silver bromide<sup>18</sup> but recent investigations of Odén have shown that the (average) dispersity always decreases as the concentration decreases, the appearance of a minimum dispersity (maximum grain size) being due to aggregation and formation of secondary particles, especially when the particle size is small—20 $\mu$ .

An important point with regard to the formation and group crystallization of the silver bromide grains of emulsions is raised in a more general connection by Svedberg.<sup>19</sup> He points out that two cases of condensation exist, *viz.*, volume condensation and surface condensation. "When solutions that react with each other are mixed, in most cases surface condensation at the contact surface between the solutions takes place. *If the condensation or the reaction proceeds slowly enough, volume condensation may occur even in this case.* Pure volume condensation most probably gives rise to systems of a more homogeneous degree of dispersion than mixed volume and surface condensation. The pure surface condensation very likely produces systems with rather unequal particles." Now we know that increasing protection with gelatin decreases the grain size, and, generally makes for a finer grained, more uniform precipitate.<sup>20</sup> The delay in the aggregation produced by the gelatin tends to convert the condensation from the surface type to the volume type. On the other hand, the important influence of the rate of addition on the dispersity and uniformity in initially gelatin-weak systems is in agreement also with Svedberg's suggestion, since by protracting the surface condensation aspect the range of grain size may be greatly extended.

I cannot delay to speak further of the other important factors operative in determining the emulsion structure. Such are, *prima facie*, the Ostwald ripening, the influence of excess bromide, of ammonia and of temperature. With the development of methods of measurement and specification of the dispersity and distribution, it is only a question of time for the predetermination of a desired distribution to be a matter of course.

<sup>18</sup> A. P. H. Trivelli and S. E. Sheppard, "Silver Bromide Grain," p. 38

<sup>19</sup> "The Formation of Colloids," p. 57, J. A. Churchill, London, 1921

<sup>20</sup> Cf. Trivelli and Sheppard, "The Silver Bromide Grain"

## PHOTOGRAPHIC CHARACTERISTIC CURVES

The characteristic curve of a negative emulsion is obtained by plotting the photometric density

$$D = -\log_{10} T, \text{ where } T = I/I_0 = \frac{\text{light transmitted}}{\text{light incident}}$$

as a function of  $\log_{10} E$ , where  $E$ , the exposure = (intensity  $\times$  time). If a series of such curves is obtained for different times of development, the resulting family takes the form in Fig. 3.

The point where the straight lines cut the axis of  $\log E$  gives the critical value  $\log i$ , and  $1/i = 1/\text{inertia}$ , the H. and D. speed.

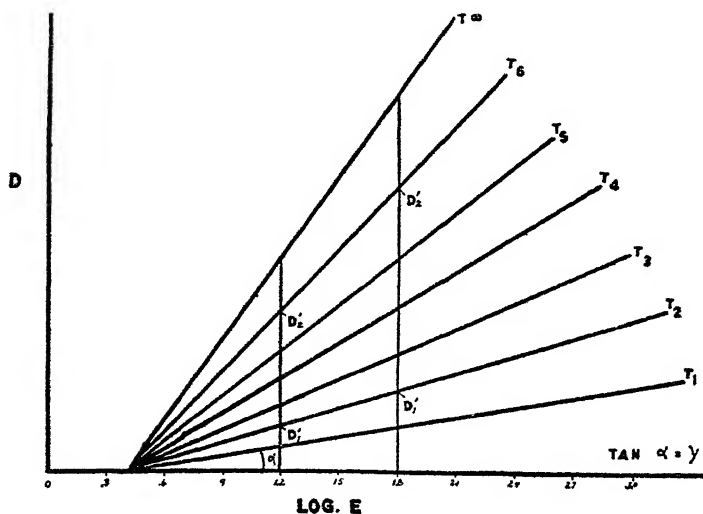


Fig. 3.

The slope of the curve gives  $\gamma$ , the development factor, or measure of contrast, and the ultimate  $\gamma$  or  $\gamma_\infty$ , the plate's capacity for contrast.

Before discussing the possible theoretical bases connecting the characteristic curve (or density-exposure function) with the dispersity-distribution of the grains, let us examine some experimentally obtained data and correlations.

For a series of commercial emulsions, the following results were obtained:<sup>21</sup>

<sup>21</sup> Cf. E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, *J. Phys. Chem.*, loc. cit.

TABLE I

TABLE I

Type of emulsion	Dispersity factors										Distribution parameters			Sensitometric parameters		
	No. grains per sq. cm.		Average size grain				Thickness in $\mu$		Ratio thickness to grain diam.	Max grain size in $\mu^2$						
			G. Ag-Hal. per $\text{cm}^2$	Equiv. diam. in $\mu$	Projected area in $\mu^2$	Equiv. vol. in $\mu^3$	For spheres	For plates		$\gamma_0$	K	$\alpha$	Speed H. & D.	$\gamma^\infty$	R	
Process A	4.3	5.12	.00084	0.38	0.115	0.030	0.39	0.26	1:1	1.2	4000	5.8	0	6	4 057	7.51
Process B	.67	.49	.00137	0.84	0.560	0.317	0.85	0.57	1:1	1.6	340	8.9	.55	7	4.956	6.21
Positive	1.85	2.13	.00087	0.70	0.390	0.073	0.52	0.19	1:38	2.2	573	2.5	....	9	4.825	5.11
Medium Speed A	2.11	1.74	.00121	0.76	0.450	0.089	0.55	0.20	1:3.8	6.2	1068	3.0	....	370	1.395	5.53
Medium Speed B	.94	.72	.00130	0.80	0.502	0.213	0.74	0.42	1:1.9	6.2	277	4.3	.53	440	1.234	2.34
Medium Speed C	1.50	.89	.00168	1.41	1.567	0.173	0.69	0.11	1:12.8	8.4	{ 222	{ 4.3	{ .79	680	1.625	5.73
											{ 32	{ 12.2	{ 1.86			
High Speed A	.66	.49	.00135	.97	0.732	0.318	0.85	0.43	1:2.2	8.6	{ 110	{ 0.95	....	1236	1.095	2.47
											{ 311	{ 3.4	....			
High Speed B	.48	.33	.00147	1.67	2.198	0.476	0.98	0.22	1:7.7	12.6	{ 200	{ 2.8	.76	2585	.93	3.73
											{ 30	{ 6.5	{ 2.05			

Note on sensitometric parameters

 $\gamma^\infty$  = maximum slope of curve $D_m$  = maximum density on exposure

R = tangent range, measure of latitude

Average per cent.

Ag-Hal. in dry emulsion

33.6, range 31.4 to 36.8

It will be seen from the table that the order of "speed" increase is on the whole in line with decreasing dispersity, or increasing grain size, but not a very definite progression. Turning to  $\gamma_{\infty}$ , the limiting slope of the straight line portion of the characteristic curve, Higson and Toy<sup>22</sup> have attempted to summarize and evaluate the factors determining this. Their extended arguments will not be dealt with here, but it may be noted that they conclude that  $\gamma_{\infty}$  decreases with increasing average grain size. The results now given partially support this, but not regularly. But, in two sets of experimental emulsions, prepared under controlled conditions with one factor varied to increase grain size and speed conjointly, the opposite result was obtained. Instead of  $\gamma_{\infty}$  decreasing with increasing grain size, it increased somewhat, and perfectly regularly. Conclusions from these latter data are probably more reliable, because the "grain sensitivity factor," to be considered shortly, is relatively constant, whereas over a series of commercial plates it varies in an arbitrary manner. Also in the experimental emulsions each plate was coated with an equal weight of silver halide per unit area, the ratio of halide to gelatin was kept constant, and hence the dispersity, as total number of grains per unit area, decreased progressively as the grain size increased. The absolute sensitivity factor, per unit area of grain, and the distribution of grain-sizes, appear to be of more importance in determining  $\gamma_{\infty}$ . Higson and Toy recall Sheppard and Mees' observation that desensitizing a plate with chromic acid increases  $\gamma_{\infty}$ . This has recently been confirmed in this laboratory, and it has also been found, by experiments with one-grain-layer plates, that the desensitizing action of chromic acid affects the smaller grains more than the larger ones. Consequently, the range of grain sizes effective in exposure is reduced, and thereby  $\gamma_{\infty}$  is increased. This is so far in agreement with another of Higson and Toy's postulates for high  $\gamma_{\infty}$ , *viz.*, restricted size range, when this is simultaneously a restricted sensitivity range.

One other important photographic characteristic which can be expressed by a sensitometric parameter is the latitude. This means the range of exposure within which the plate will give correctly exposed pictures. The projection of the straight

<sup>22</sup> *Phot. J.*, **63**, 68 (1923)

line portion of the curve on the  $\log E$  axis measures this, but is difficult to define, and Ross<sup>23</sup> has suggested that a better measure is the "range" or "tangent range," illustrated in Fig. 4, *i. e.*, the intercept of the tangent through the inflection point of the curve in the  $\log E$  line and in the line through  $D_m$ . Here again, while the "range" is lower for the finer grained process emulsions than for the medium and high speed groups, there is no definite progression in the groups themselves. In the experimental sets, however, the "range" and latitude increase steadily with the grain size, and therewith with the range of

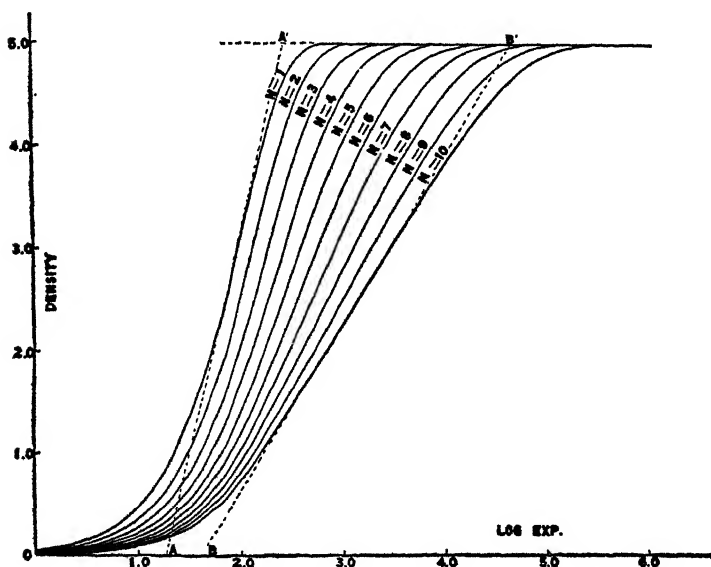


Fig. 4.

grain sizes. That is, the distribution parameter  $k$  is the best criterion here; this falls steadily as the latitude increases. To indicate this more clearly, the tables and a figure from a paper<sup>24</sup> describing these experiments are reproduced here.

#### THEORY OF DENSITY-EXPOSURE FUNCTION

So far only the empirical, or to use a name that is still honorable, experimental correlation of dispersity characteristics and

<sup>23</sup> F. E. Ross, *J. Opt. Soc. Am.*, **4**, 255 (1920)

<sup>24</sup> *J. Phys. Chem.*, in press

TABLE II  
GRAIN CHARACTERISTICS OF WC SERIES

Average size grain														
No.	$N \times 10^{-3}$ grains on original	$\# \times 10^{-1}$ grains on 1-layer	$G$ , AgBr/cm <sup>2</sup> , original plate	% Conc. AgBr per cm <sup>2</sup> , original plate	Average size grain		$\#$ (obs.) in $\mu^2$	$\#$ (calc.) in $\mu^2$	$D$ (obs.) in $\mu$	In plates	In $\mu$ spheres	Approx.		
					$W$ , in g. $\times 10^{12}$	$V$ , in $\mu^2 \times 10$								
6	102.2	7.15	0.001798	31.34	0.174	0.272	0.186	0.183	0.487	0.145	0.373	1:3.5		
7	38.0	6.65	0.001798	31.34	0.473	0.731	0.276	0.276	0.593	0.265	0.519	1:2.2		
8	15.5	5.42	0.001798	31.34	0.160	1.793	0.398	0.474	0.712	0.451	0.699	1:1.6		
9	12.8	2.23	0.001798	31.34	1.405	2.171	0.637	0.604	0.900	0.340	0.746	1:2.6		
10	8.01	2.80	0.001798	31.34	2.244	3.476	0.655	0.596	0.908	0.529	0.872	1:1.7		
11	7.65	2.67	0.001798	31.34	2.350	3.632	0.776	0.760	1.011	0.468	0.885	1:2.2		
12	5.71	2.00	0.001798	31.34	3.150	4.866	1.110	1.040	1.190	0.440	0.976	1:2.7		

No.	No. grains meas.	Max. grain size obs in $\mu^2$	Total area grains per cm <sup>2</sup> , orig plate in $\mu^2 \times 10^{-3}$		Total area grains per cm <sup>2</sup> , 1-layer plate in $\mu^2 \times 10^{-3}$		%	$k$	$\alpha$	r. p. $\mu$ resolving power	Turbidity
			From mean		From mean						
6	1042	1.3	19.01	18.67	0.131	0.131	1255.6	6.13	.....	59	8.1
7	1018	1.3	10.49	9.79	0.184	0.171	670.0	3.67	.....	47	8.5
8	1035	2.1	7.35	8.13	0.257	0.284	290.0	1.53	0.041	37	9.9
9	1930	3.9	7.73	7.65	0.135	0.133	190.8	1.37	0.293	38	9.9
10	940	3.5	4.77	4.56	0.167	0.159	186.0	1.44	0.300	37	11.4
11	1026	4.5	5.81	5.84	0.203	0.214	165.0	1.21	0.523	40	12.4
12	3154	4.9	5.94	5.99	0.208	0.210	120.0	0.81	0.820	37	11.3



photographic characteristics, has been dealt with. How far is a basic theory possible? This is too large a question, and too unsettled yet to answer here. But we may look into some aspects of it. If we construct from the density-exposure function, or, graphically, from the actual density-log  $E$  curve, its first derivative (cf. Fig. 6) we obtain a curve which expresses the amount of substance changed per unit time,  $\Delta x/\Delta t$ , plotted against time—or, in the present case,  $dD/d \log E$  against  $\log E$ . This curve is analogous to the "mortality curve" of vital statistics. Now, under certain conditions this *rate* (or mortality) curve can be identified with the variation (frequency) curve

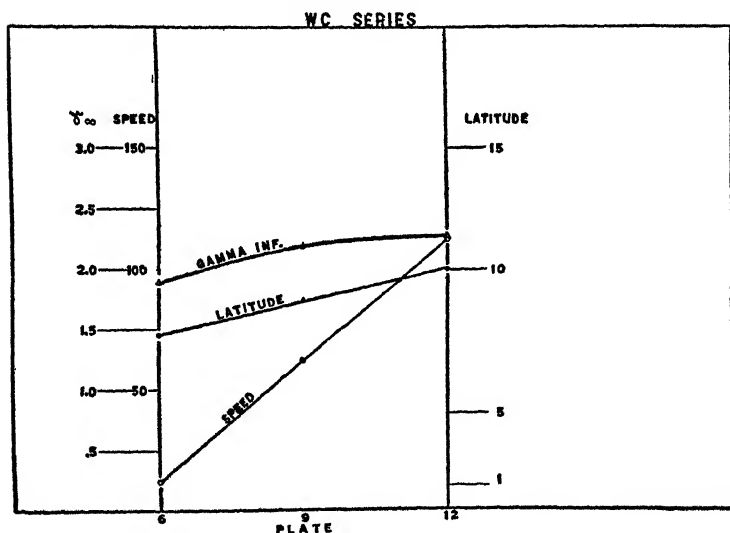


Fig. 5.

of individual inertias (reciprocals of sensitivity).<sup>25</sup> In the case of a multi-grained layer exposed to light, it is evident that the reduction of intensity through the film introduces a complication in that effectively, grains at a lower level will act as if of lower sensitivity. But *this relation shows in a direct manner the way in which the size-frequency distribution must determine the density-exposure function, and thereby the characteristic curve.* The simplest hypothesis possible, is that the sensitivity is directly

proportional to the grain size (projective area) in one and the same emulsion. This hypothesis was tested, with one-grain layers, by the author and his collaborators,<sup>26</sup> but found to be inadequate. The problems which have to be overcome before the broad relation noted above can be applied, will now be discussed.

#### THE DISPERSION OF SENSITIVITY IN GRAINS OF ONE SIZE

In the important paper cited Svedberg<sup>27</sup> showed that, (a) the form of the density-exposure function could not be determined

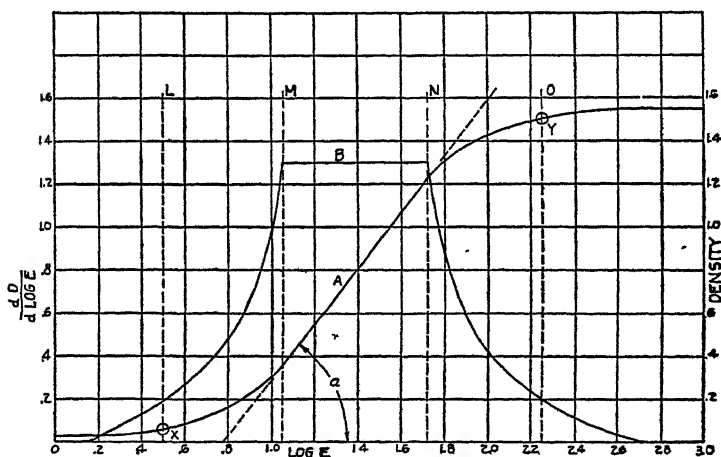


Fig. 6.

solely by light-absorption in a multi-grain layer, because one-grain layers give gradation (b) could not be due to distribution of grain sizes alone, because grains of the same class size (projective area) give variable sensitivity, *i. e.*, give gradation.

This last important result was confirmed with great precision by Toy<sup>28</sup> for grains of the same size, shape, and orientation. Hence, it has to be assumed, as suggested by the author and his collaborators in a paper on the subject<sup>29</sup> that in any class size

<sup>26</sup> E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, *J. Phys. Chem.*, **27**, 141 (1923)

<sup>27</sup> *Loc. cit.*

<sup>28</sup> *Phot. J.*, **61**, 417 (1921)

<sup>29</sup> E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, "Studies in Photographic Sensitivity," *J. Franklin Inst.*, **194**, 501 (1922)

sensitivity is distributed according to some probability function.

Now a random distribution of sensitivity among grains of one size might be due:

- (a) to inherent variation of sensitivity, due to conditions in emulsification
- (b) to non-continuous, quantum distribution of energy in light.

The latter hypothesis was referred to by Svedberg<sup>30</sup> and mathematically developed by Silberstein,<sup>31</sup> on the basis that one quantum, or "light dart" encountering a grain fully, made it developable. The formula obtained

$$\frac{x}{N} = 1 - e^{-na} \quad (6)$$

where  $N$  = no. of grains per unit area

$x$  = no. of grains made developable

$a$  = area of grain

$n$  = number of quanta incident per unit area

was tested on experimental data of Trivelli and Righter<sup>32</sup> and good agreement obtained. However, it was early evident that some other factor for "inherent sensitivity" not given in Silberstein's early hypothesis, must be assumed. The author pointed out that desensitization, by chromic acid, etc., left the projective area of the grains unchanged. Furthermore, Jones and Schoen<sup>33</sup> found that the energy incident in Trivelli and Righter's experiments was much more than that equivalent to one quantum per grain:

TABLE III

Diameter $\mu$	Area $\mu^2$	Quanta (420 $\mu$ ) per grain
0.25	0.0494	$2.0 \times 10^1$
0.50	0.196	$7.8 \times 10^1$
1.00	0.787	$3.1 \times 10^2$
2.00	3.14	$1.25 \times 10^3$
3.00	7.08	$2.83 \times 10^3$
4.00	12.6	$5.05 \times 10^3$

<sup>30</sup> *Phot. J.*, **61**, 332 (1921)

<sup>31</sup> *Phil. Mag.*, **44**, 257 (1922)

<sup>32</sup> *Phil. Mag.*, **44**, 252 (1922)

<sup>33</sup> *J. Opt. Soc. Am.*, **7**, 213 (1923)

In view of these facts, Silberstein<sup>34</sup> has modified his theory by the conception that not the whole area of the grain is vulnerable to quantum impact, but only a fraction  $\epsilon a$ . This fraction is further supposed to be split up into "sensitive spots" distributed at random over the grain surface such that  $\epsilon = \bar{k} \bar{\omega}$ , where  $\bar{k}$  = average number of spots per grain,  $\bar{\omega}$  average area of a spot. The formula becomes

$$\frac{x}{N} = 1 - e^{-\bar{K}(e^{-\bar{n}\bar{\omega}} - 1)} \quad (7)$$

whence

$$\log \frac{N}{N-a} = \bar{K}(1 - e^{-\bar{n}\bar{\omega}}) \quad (8)$$

The modified formula is being tested, but it may be noted that an integrated form has been applied successfully by Silberstein to X-ray density exposure data.

The elementary formula taken for grains of one class size  $a$  is the quantum formula (6), modified by the considerations just discussed to include  $\epsilon$ , the sensitive quotient, of area, assumed constant, i. e.,

$$x = N(1 - e^{-\epsilon na}) \quad (9)$$

The number of grains of size  $a$  to  $a + da$  is  $N_a da = f(a) da$ , where  $f(a)$  is the distribution function. If this be of exponential form

$$f(a) = C e^{-\mu a} \quad (10)$$

written thus, but equivalent to (3) and valid from  $a = a_1$  to  $a = a_2$  (and negligible outside these limits), then the total projected area of AgBr made developable will be

$$K = A - \frac{A\mu^2}{(\epsilon n + \mu)^2} \left[ [1 + (\epsilon n + \mu)a] e^{-(\mu + \epsilon n)a} \right]_{a_2}^{a_1} \quad (11)$$

where  $A = \int af(a)da$  is the total available area of silver bromide.

If the frequency curve, as often happens, has a long "tail," we can approximate by putting  $a_2 = \infty$ , while if  $a_1$  is small

<sup>34</sup> *Phil. Mag.*, [III] 45, 1062 (1923). This is an interesting example of the derivation of the density exposure function, i. e., the characteristic curve from the size-frequency, or distribution curve, by integration over this, assuming a specific fundamental reaction, in this case, a quantum hypothesis. It is, therefore, important, if only as a preliminary model, and I have therefore quoted it somewhat fully

enough, a permissible simplification consists in putting  $a_1 = 0$ . Thus the formula becomes

$$K = A - \frac{A\mu^2}{(\epsilon n + \mu)^2} \quad (12)$$

Using the generally assumed relation between photographic density  $D$  and mass of developed silver halide<sup>35</sup> this may be written

$$D = D_m \left( 1 - \frac{\mu^2}{(\epsilon n + \mu)^2} \right) \quad (13)$$

But for one-grained layers, and, very possibly for plates exposed to X-rays, which may be regarded, owing to negligible absorption, as equivalent, the theoretical derivation of the density-opacity relation would not give this proportionality, but only for multi-grained layers.<sup>36</sup> For one-grained layers the correct relation becomes

$$T(\text{transparency}) = 1 - K, \text{ whence}$$

$$D = \log \left( \frac{1}{T} \right) = -\log (1 - K) \quad (14)$$

Silberstein has combined this relation with the formula (12), for the *developed* area  $K$ .<sup>37</sup> Using the abbreviation

$$\frac{\epsilon n}{\mu} = \alpha E \quad (15)$$

There is obtained the density-exposure function

$$D = -\log \left( 1 - K_m + \frac{K_m}{(1 + \alpha E)^2} \right) \quad (16)$$

where  $K_m$  is defined by

$$D_m = -\log (1 - K_m) \quad (16a)$$

In most practical cases  $D_m$  generally exceeds 3, so that  $(1 - K_m) < 0.001$ . In such cases, we may use the limit of (16) for  $K_m = 1$  (*i. e.*, for  $D_m = \infty$ ), whereby

$$D = 2 \log (1 + \alpha E) \quad (17)$$

Silberstein has compared this simplified formula with results of X-ray exposures by R. B. Wilsey on "portrait film" with the following results.

<sup>35</sup>  $D = p$  (mass of silver); cf. Sheppard and Mees, "Investigations," p. 38

<sup>36</sup> Cf. P. G. Nutting, *Phil. Mag.*, **26**, 423 (1913)

<sup>37</sup> Permissible for *exposure* to X-ray. This seems somewhat questionable for the photometry of the developed grains, in multi-grained layers, by ordinary light

TABLE IV

<i>E</i>	<i>D</i> <sub>obs</sub>	<i>D</i> <sub>calc.</sub>	$\Delta D$
1	0.08	0.12	+0.04
$\sqrt{2}$	0.15	0.17	+0.02
2	0.20	0.23	+0.03
$2\sqrt{2}$	0.29	0.30	+0.01
4	0.40	0.41	+0.01
$4\sqrt{2}$	0.54	0.54	0.00
8	0.72	0.69	-0.03
$8\sqrt{2}$	0.90	0.87	-0.03
16	1.10	1.07	-0.03
$16\sqrt{2}$	1.32	1.29	-0.03
32	1.56	1.53	-0.03
$32\sqrt{2}$	1.80	1.79	-0.01
64	2.12	2.06	-0.06
$64\sqrt{2}$	2.48	2.33	-0.15

The existence of "sensitive spots" was independently and directly demonstrated by Svedberg.<sup>38</sup> He showed that the "initial development centers," first observed by M. B. Hodgson<sup>39</sup> were distributed at random for any class size of grain. Svedberg suggested that the true measure of sensitivity is the number of "centers" per unit grain area—grains not differing from each other except in regard to the number of sensitive spots per unit area. Apparent growth of sensitivity with grain size is then limited to this factor.

This conclusion does not seem to agree with the relatively greater resistance of the sensitivity on large grains (to chromic acid) than on smaller ones, which we have recently established.<sup>40</sup> It appears to us that the inherent sensitivity of the grains must differ progressively with the size. It appears possible that, whatever its nature, it is aggregated and held more tenaciously in the larger grains, possibly in larger aggregates. The possibility that the sensitivity is due to colloid silver, in a microscopic nuclei insufficient to initiate development, is supported by a recent observation made by E. P. Wightman and the author. We have found that in certain emulsions a large part of the "sensitivity" destroyed by chromic acid, can be regenerated by treatment with potassium iodide. This is quite

<sup>38</sup> *Phot. J.*, July, 1922

<sup>39</sup> *J. Franklin Inst.*, 184, 705 (1917)

<sup>40</sup> In press

analogous to the regeneration of the latent image by such nucleus exposure methods (due to Lippo-Cramer) and points to the "latent image" and "sensitivity" being of like nature. The colloid silver would be produced by weak reducing substances derived from the gelatin, and accounting for the different photographic properties of gelatins,<sup>41</sup> when taken in conjunction with desensitizing impurities also present.

We can now partially answer the question, is grain size a necessary and sufficient condition for sensitivity? It is not a sufficient condition, but it is most probably a necessary one. This may be due entirely to an unknown factor for higher inherent sensitivity of the sensitive nuclei in large grains or may be accounted for on a quantum theory of exposure. If the S-shaped curves for number of grains made developable as function of exposure, for a single class size observed by Svedberg<sup>42</sup> and others, for low sensitivity grains are confirmed, the quantum hypothesis would have to be still further modified; possibly, as suggested by Prof. Svedberg himself, by requiring several quanta to fall within a limited area of the grain, a condition which should be capable of test by comparing X-ray exposures with blue light exposures. But, in any case, it appears that the study of the dispersity of silver halides in relation to photographic sensitivity leads us to a study now commenced, of the dispersity of photographic sensitivity—perhaps colloid silver, perhaps something from gelatin—in the individual silver halide grains. There are wheels within wheels, and since the atom itself is now recognized to be a disperse system, we may have to follow through into the silver atom itself.

#### DISCUSSION ON S. E. SHEPPARD'S PAPER

### DISPERSITY OF SILVER HALIDES IN RELATION TO THEIR PHOTOGRAPHIC BEHAVIOR

T. SVEDBERG: I think we have all listened to Dr. Sheppard's paper with the greatest interest. This is a subject to which Dr. Sheppard himself has contributed very much valuable information. It is a sample of the extremely fine experimental

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<sup>41</sup> Cf. B. V. Storr, *Ann. Rep. Soc. Chem. Ind.*, **37**, 465 (1918); S. E. Sheppard, "Gelatin in Photography," Vol. I, p. 49 (1923)

<sup>42</sup> *Phot. J.*, **61**, 332 (1921)

work now being done in the Eastman laboratory. If I understood Dr. Sheppard correctly, he said that there were not data enough available to enable us to decide between the quantum theory and the theory of the pre-existence of the centers in the silver halide grains.

S. E. SHEPPARD: Hardly sufficient, I think. It is possible that there may never be a complete solution distinguishing between the two. This photographic investigation is an important thing in a way that many other such investigations are not, for the quantum theory is important. Yet it would obviously be impossible to base it on that alone. If the evidence were so good that it was practically conclusive, it would still be necessary to make the theory acceptable to the majority of the physicists and chemists. Therefore it is the collateral evidence there and the bulk of other evidence in the other directions that will decide the matter. But the photographic end is interesting in offering one way of attacking the problem. But the fact that there is an inherent sensitivity in the grains is an outstanding difficulty for the pure quantum theory of exposure.

J. ALEXANDER: I think we all have to thank Dr. Sheppard for having brought out in very important language a thing which is very frequently overlooked, and that is that in the structure of matter we do not go continuously from atoms or molecules into visible particles but that there seem to be series of successive steps. As a consequence you see a great deal of stress being placed nowadays on the so-called primary and secondary particles. This very interesting and valuable work that has been done by the photographic men clearly brings out the very great importance of these successive groupings that occur not only in photographic conditions but also seem to be a very general condition that occurs in all aspects regarding the bodies which are now visible. Recently looking at some slides of tanned skins, first in the microscope and then in the ultra-microscope very great differences were evident between them. I would like to ask, has anything been done toward the ultra-microscopic examination of these silver grains?

S. E. SHEPPARD: A little work has been done, but up to the present time very little, for this reason, that ultra-microscopic examination of the silver bromide grain means using an intensity



of light, such that the conditions that we are looking for are obliterated or are only evident chemically. We do not know whether the change that takes place is exactly or approximately proportionate to the change which takes place in the dispersity of the invisible.

[CONTRIBUTION FROM THE SOILS LABORATORY AGRICULTURAL  
EXPERIMENT STATION, UNIVERSITY OF MISSOURI]

## THE NATURE OF THE CHEMICAL REACTIONS OF COLLOIDAL CLAY

BY RICHARD BRADFELD

Soils have been known to possess colloidal properties from the days of van Bemmelen. Since that time most every property of soils, chemical or physical, which did not seem in harmony with expectations, has been laid at the door of soil colloids. Such procedure was quite safe because no one had ever isolated the colloidal fraction of soils in quantities sufficient to make a thorough study of its properties and consequently was unable to deny any property attributed to it. The situation was very well summarized a few years ago by Prof. Emil Truog when he said, "Various properties having no existence in either pure chemistry or physics are ascribed to colloids in order that certain phenomena may be explained without going to the trouble to find the real cause."<sup>1</sup>

This earlier work on soil colloids was done by indirect methods on the soil itself. The soil system is exceedingly complex. The great bulk of it is made up of relatively large, inert mineral fragments. The colloidal fraction forms a coating of varying thickness upon part or all of this larger inert fraction. Such methods were of necessity only qualitative. Rough distinctions could be made but progress in the study of the fundamental properties of the colloidal material was retarded by the lack of a satisfactory method for separating it from the non-colloidal fraction.

Two rather similar methods have recently been developed which are fairly satisfactory. Fry, Middleton and Moore of the Federal Bureau of Soils,<sup>2</sup> suspend the colloidal material by agitating the air dry soil in a barrel churn with five parts of distilled water and sufficient ammonia to deflocculate it. The coarser particles are allowed to settle out by gravity for 24 hours. The material remaining in suspension is then passed through a Sharples supercentrifuge at such a rate that all particles 1 micron and over in diameter are thrown out of suspension. The

<sup>1</sup> Truog, E., *J. Phys. Chem.*, **20**, 482 (1916)

<sup>2</sup> Fry, Middleton and Moore, *J. Ind. Eng. Chem.*, **13**, 527-30 (1921)

"ultra-clay" is then removed by passing that portion still in suspension through a Pasteur-Chamberlain filter. All the particles less than 1 micron in diameter are deposited together on the walls of the filter tube.

In the method developed independently and at about the same time at the Soils Laboratory of the Missouri Agricultural Experiment Station, the fresh soil is used instead of the air-dried and the use of a deflocculant is dispensed with.<sup>3</sup> The addition of any alkali in sufficient quantities to thoroughly deflocculate an air-dried soil materially alters the natural properties of the colloidal fraction. The coarse non-colloidal material is removed by the same procedure used by the Bureau of Soils investigators. The suspension coming from the centrifuge the first time, which contains only the fraction whose particles are less than one micron in diameter, and which is separated by the Pasteur-Chamberlain filter and termed "ultra-clay" by Fry, Middleton and Moore, is, with the soils studied, distinctly heterogeneous. It is passed through the supercentrifuge a second time at the rate of 350 cc. per minute. The fraction still remaining in suspension contains no particles large enough to be visible in the direct vision, high powered microscope. It forms a solution which shows no tendency whatsoever to settle out on prolonged standing and appears clear when examined by transmitted light and turbid by reflected light. When a dilute solution is desired this fraction can be used just as it comes from the centrifuge the second time. If a concentrated sample is desired it may then be filtered by the Pasteur-Chamberlain filter or passed through the supercentrifuge a third time at the rate of 2-3 liters per hour. This prolonged application of a centrifugal force of about 30,000 times gravity is sufficient to deposit almost all of the colloidal clay on a celluloid sleeve placed inside the centrifuge bowl. At the end of a run the sleeve may be removed and the colloidal clay now having much the consistency and appearance of ordinary axle grease, removed by means of a spatula.

This colloidal fraction is distinctly higher than the rest of the soil in  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{H}_2\text{O}$ , both combined and hygroscopic, and distinctly lower in  $\text{SiO}_2$ . Practically all of the  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in the clays studied is soluble in hot concen-

<sup>3</sup> Bradfield, R., *Missouri Agr. Ex. Sta. Research Bull.*, 60 (1923)

trated HCl. The great solubility indicated that it might be made up largely of a mixture of the completely broken down end products of weathering, *e. g.*, colloidal  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , but a series of comparative tests with a synthetic mixture of these colloids having a similar total analysis, indicates that the natural colloidal clay, especially that extracted from the Putnam clay, is a complex acid aluminosilicate or more probably a mixture of closely related complex aluminosilicates.<sup>4</sup>

Preliminary flocculation studies with a wide variety of electrolytes showed that the usual valence relations held. The trivalent Al was by far the most efficient flocculant, the divalent alkali earths were next and the neutral salts of the alkali metals next. The alkaline salts of the alkali metals caused flocculation only at relatively high concentrations. This was especially true of the basic phosphates. In order to find out whether the abnormally high requirement in the case of the basic phosphates was due to its buffer action or to some specific effect of the phosphate ion, a study was made of the variation in the amount of K required to flocculate the acid colloidal clay at different H ion concentrations. The K mixtures with Sørensen values less than 6 were prepared by adding graded amounts of HCl to constant quantities of a standard KCl solution and diluting to constant volume. The mixtures with Sørensen values greater than 7 were obtained by combining standard solutions of KCl and KOH in different proportions, thus varying the H ion concentration but keeping the K content constant. The electrolyte requirement was determined by the usual "trial and error" method. After the critical concentration had been carefully located for each mixture, the Sørensen value of the supernatant liquid was measured electrometrically. The results of this study are presented graphically in Fig. 1. The electrolyte requirement increases gradually with a decrease in the hydrogen ion concentration until the neutral point is reached, increases ten-fold very quickly, then becomes constant. Variations in Sørensen values between 8.5 and 12 had no effect whatever upon the electrolyte requirement. With KCl alone, only 1.4 milliequivalents of K were required, with KOH alone, 14.0 milliequivalents, yet a mixture made up of 9 parts KCl and 1 part KOH had the same requirement as the KOH alone.

<sup>4</sup> Bradfield, R., *Missouri Agr. Ex. Sta. Research Bull.*, 60 (1923)

The sudden change in electrolyte requirement at the neutral point is suggestive of a titration curve of an acid by a base. As the neutral point is approached only a few drops of alkali are necessary to shift the Sørensen value from the acid region to the distinctly alkaline zone. The fact that the electrolyte requirement is constant after sufficient alkali to produce a  $p_H$  value of 8.5 has been added, would seem to indicate that we were dealing with a definite chemical compound in this region.

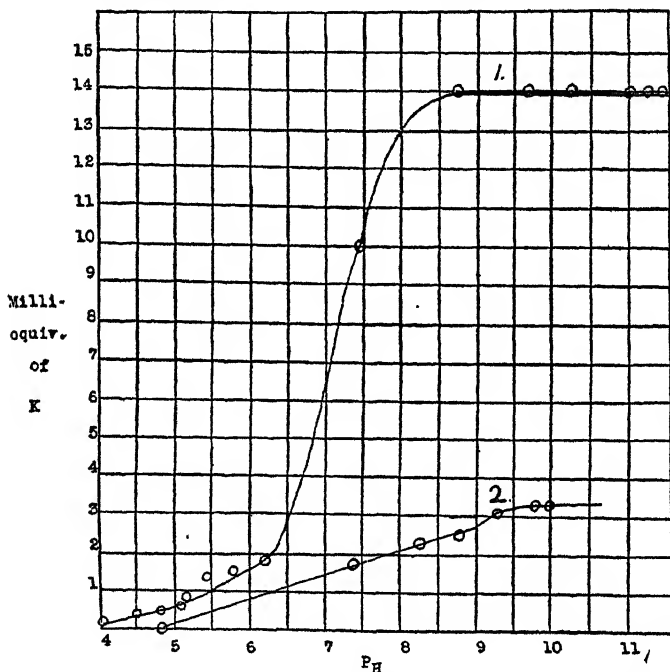


Fig. 1.—The effect of H ion concentration upon the flocculation of an acid (1) and a neutral (2) colloidal clay.

Since this compound was obtained by treating an acid colloidal clay, which we may designate as  $HX$ , with a dilute  $KOH$  solution it would seem quite natural to expect an ordinary neutralization,  $HX + KOH = KX + H_2O$  with the formation of the  $K$ -salt of the clay acid and  $H_2O$ . If this be true it would seem probable that such flocculation studies might be used for determining the end-point in the titration of the weak colloidal clay acid by an alkali. If the constancy in electrolyte require-

ment at and above certain  $p_H$  values be due to the formation of a definite salt, the amount of hydroxide required to bring the colloid to this zone of constant electrolyte requirement should be approximately the amount required for the neutralization of the colloidal acid. If we take the above curve for example, we find that 14 milliequivalents of K were required for flocculation in the case of a mixture composed of 9 parts KCl and 1 part KOH. One-tenth of this total amount of K required was in the form of KOH, hence the amount of alkali necessary for neutralization was equal to or less than 1.4 milliequivalents. A mixture of 1 part KOH and 19 parts KCl produced flocculation at 10 milliequivalents of K. In this case 0.5 of a milliequivalent of KOH was used. The true end-point is between these two values with the probability that it is somewhat closer to 0.5 than to 1.4 since the electrolyte requirement in the case of the former is 10 and since the curve is very steep in this region. Conductivity measurements to be considered later indicate that the end-point was reached when 0.66 milliequivalents of base had been added. Similar flocculation studies in which various mixtures of  $\text{CaCl}_2$  and  $\text{Ca}(\text{OH})_2$  were used yield the same type of curve and indicate the formation of a definite Ca salt when an amount of  $\text{Ca}(\text{OH})_2$  roughly equivalent to that found above was used. The total electrolyte requirement in the case of the Ca mixtures was much lower. In the region of constant electrolyte requirement only 1.5 milliequivalents of Ca were required, due no doubt to the greater insolubility of the Ca salt, but the amount of alkali required to reach this region was approximately the same.

If the sudden change in electrolyte requirement which was noticed in the acid colloidal clay when the neutral point was passed was due to a true neutralization we would expect that a neutral clay would show no such changes. The lower curve in Fig. 1 represents the electrolyte requirement of an approximately neutral clay with the KCl-KOH mixtures. The amount of KOH required was greater than the amount of KCl indicating, as we might expect, that not quite all the acid was neutralized at the natural Sørensen value, which was about 7.11, but when compared with the corresponding change in the acid soil, that of the neutral clay was relatively small.

The problem of soil acidity has probably been investigated

more than any one soil problem, but in spite of the vast amount of work that has been done there is still some doubt as to its real nature. A survey of the literature shows that the following points are very well established regardless of the nature of the underlying causes.

1. Natural soils vary in  $p_H$  value from about 3.5 to 9.5.
2. Aqueous extracts of acid soils when freed from  $CO_2$  are usually acid free.
3. Extracts of acid soils made with neutral salt solutions show a higher  $p_H$  value than the soil and also considerable titrable acidity.
4. Titration curves made by adding increments of bases to a fixed weight of soil and determining the corresponding  $p_H$  value show no definite breaks to indicate end-points, but are almost linear.
5. The slope of the curve varies widely with soil type. It is usually inversely proportional to the content of colloidal material. In other words, the buffer action of a soil is some direct function of its colloid content.

In a recent study of the effect of the soil-water ratio upon the H ion concentration of the mixtures, Salter and Morgan<sup>5</sup> found with most of the soils studied an exponential relation which could be made to fit the adsorption isotherm of Freundlich. Since some of the solid phase remained undissolved at all dilutions they conclude that their results "discredit any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, either organic or inorganic which must, under conditions of equilibrium, form a saturated solution and give an approximately constant H ion concentration" (p. 123). They believe instead that the acidity is due to the preferential adsorption of the OH ion by the soil colloids.

This conclusion is directly opposed to the results cited above, which tend to show that the colloidal material of acid soils is in every respect a true acid. An analysis of the data and the arguments of Salter and Morgan reveals the possible cause of the discrepancy. Their work was done on soils. As pointed out above, soils are extremely complex systems made up largely of relatively coarse, inert mineral fragments. The amount of the

<sup>5</sup> Salter and Morgan, *J. Phys. Chem.*, **27**, 117-40 (1923)

more active colloidal material is relatively small, especially in soils of light to medium texture. The fact that some of these larger inert particles remained undissolved in all the soil-water ratios does not indicate necessarily that the solutions were saturated with an acid. In fact it would seem highly improbable that if the acidity of soils is due largely to complex colloidal acids, that even a concentration of 1 part soil to 1 part water would be saturated with it. Salter and Morgan's curves are apparently beginning to approach constancy. It is interesting to note also that the two soils which seem to them to be abnormal and for which it was "impossible to calculate an adsorption isotherm which would satisfy any three points on the curve" were the only clays and consequently the only highly colloidal soils studied. This would seem to indicate that in the case of these soils the concentration of the colloidal acid was sufficiently great to approach rather closely the point at which the H ion concentration would become practically constant. If their failure to reach a fairly constant H ion concentration was due to the low colloid content of the soils studied, it would appear that if the colloidal fraction of an acid soil were extracted and concentrated and the effect of dilution upon this concentrated colloidal solution studied, that the concentration required to give an approximately constant Sørensen value could be determined.

An acid colloidal clay solution containing 12.8% oven-dried material was prepared and from it dilutions containing 6.4%, 3.2%, 1.6%, 0.8%, 0.4%, 0.2%, 0.1%, 0.05%, and 0.025% were made. The H ion concentration of each was measured electrometrically. A similar series of dilutions was made with acetic acid, starting with a 0.1078 *N* solution. The results of this study are plotted in Fig. 2. The portion of the colloidal clay curve for concentrations up to 2-3% is almost identical in form with those of Salter and Morgan. With higher concentrations the curve flattens and the  $p_H$  value becomes almost constant. The similarity between the acetic acid and the colloidal clay curves is so striking as to make it seem highly improbable that in the case of the former we are dealing with a true acid and in the case of the latter, not with an acid, but an adsorption compound. The colloid content of most soils is so low that it is probably only in the exceptionally heavy clays that the flat region of the curve is reached, even at the 1 : 1 soil-water ratio.



The differences in the Sørensen values yielded by the two acids are due to differences in their strength, the colloidal clay acid being a much weaker acid than acetic. The fact that one is

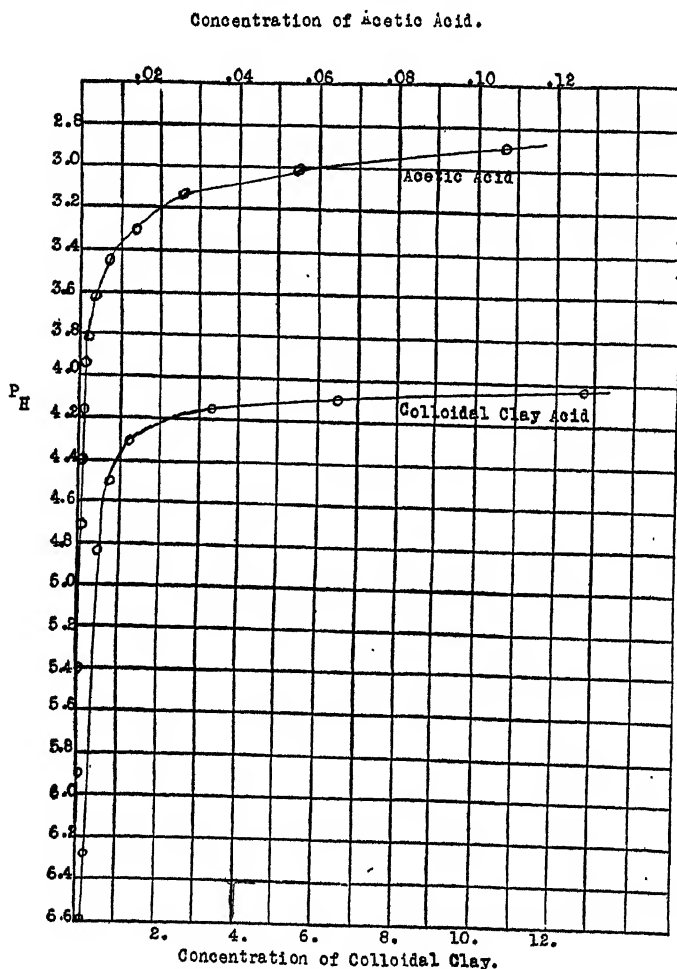


Fig. 2.—The effect of concentration of colloidal clay and acetic acid upon H ion concentration.

colloidal and the other crystalloidal is due merely to differences in the complexity of their molecules and not to any fundamental difference in the nature of their acidity.

of soil acidity are: (1) No one has ever been able to isolate an undeniable acid from a soil in quantities commensurate with the soil's sourness.<sup>6</sup> (2) Acid soils do not absorb bases in equivalent quantities. (3) Titration curves made by titrating a comparatively large mass of soil with a base are practically linear, showing no break such as is characteristic of true neutralizations.

The data presented thus far indicate that the colloidal clay of acid soils is a true acid and it is known to exist in quantities that are commensurate with the soil's sourness.

The fact that titration curves of soils may show no breaks may be due to the experimental procedure usually followed. It is much more convenient to add increments of a solution of a standard base to a weighed sample of an air-dried soil than it is to reverse the operation and titrate a definite amount of the standard base with weighed increments of the dry soil. For that reason, probably, most titration curves of soils are made by titrating the extremely weak soil acid with increments of the strong base. Such a procedure is contrary to the precepts of physical chemistry. Under such conditions, the substances responsible for the strong buffer action, the weak acid and its salt, are present from the start of the titration in maximum quantity and they tend to obscure any break that might otherwise be shown. The colloidal clay acid lends itself very nicely to the reverse titration, 1% solutions can be measured readily with a burette. 10 cc. of 0.01 *N* solutions of NaOH and Ca(OH)<sub>2</sub> were placed in a series of 100 cc. flasks, and a 1% solution of the acid clay added in 10 cc. increments. All solutions were then made up to the constant volume 100 cc. The conductivity of each series was measured and the H ion concentration determined electrometrically. The data are plotted in Fig. 3. The upper curves represent the H electrode measurements, the lower curves, the conductivity measurements. The curves are exactly of the type we would expect if we were dealing with the neutralization of a strong base by a weak acid. The conductivity shows a regular decrease for the first few additions of the colloidal acid, then becomes constant. The acid is a weaker electrolyte than its salt, consequently the ad-

<sup>6</sup> Russell, E. J., "Soil Conditions and Plant Growth," Longmans, Green and Co., London 1921. p. 110

dition of an excess causes no increase in conductivity. The neutral point is indicated by the intersection of the two portions of the curve. This intersection occurs at the point corresponding to approximately the same amount of the colloidal acid in the case of both NaOH and  $\text{Ca}(\text{OH})_2$ , which indicates that the reaction is stoichiometric. The NaOH curve is higher because the sodium salt is more soluble than the corresponding calcium salt.

The curves obtained with the hydrogen electrode are also of the type commonly obtained in the neutralization of a strong base by a weak acid. The flatter portion of the curves in the

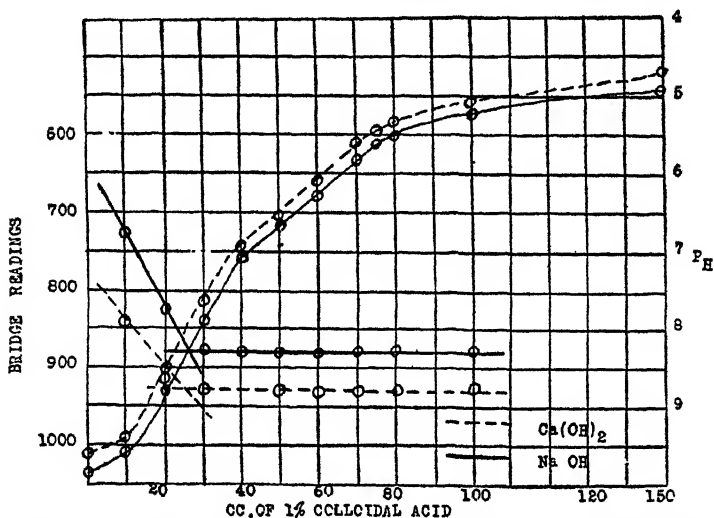


Fig. 3.—Titration curves for Putnam clay. Lower curves, conductivity method. Upper curves, H electrode method.

almost alkaline region is not so pronounced as most titration curves, probably due largely to the great dilution of the standard alkali used, which was only 0.001 *N* after dilution. In all soils studied there is a distinct change in the slope of the curves at about  $p_H$  7. This change is more marked in some soils than others and would seem to indicate that at least a di-basic acid is involved. The curves gradually flatten as an excess of the colloidal acid is added and approach the Sørensen value of the pure acid. The NaOH curve follows the  $\text{Ca}(\text{OH})_2$  curve so closely at all points as to leave no doubt about the stoichio-

metric character of the reaction. Similar curves have been made for the colloidal material of 6 acid soils taken from different sections of Missouri and having widely different origins. They are all of the same general type and indicate that the 1% solutions of the acid colloidal clays may have normalities of from 0.002 to 0.004.

These titration curves seem to answer the remaining objections to the colloidal acid theory of soil acidity. They show (1) that if the proper experimental procedure is followed, definite end-points may be obtained by both the conductivity and the hydrogen electrode method and (2) that stoichiometric quantities of different bases are required to reach that end-point.

All of the above data indicate that the colloidal clay of an acid soil is a true acid which ionizes to produce a definite H ion concentration which varies in the usual manner on dilution. Cataphoresis studies show that the colloidal particles are negatively charged and that they have a velocity of migration which is of the same order of magnitude as large slow-moving ions. The data indicate that these colloidal particles may be in fact large complex ions. If they are very large complex negative ions the strength of their charge should vary directly with the number of positive ions liberated. The velocity of migration in an electric field should be at least a relative measure of the strength of the charges. If we are dealing with a true ionization we would expect a series of mass action relations,

$$\frac{(H^+) (X')}{(HX)_n} = K_a, K_b, K_c, \dots K_n.$$

to hold. If a strong acid, which would supply the common H ion were added to the weak colloidal acids, we would expect that mere traces of such an acid would repress the ionization of the weak colloidal acids in the order of their strength and that slightly larger concentrations would repress it completely and render the complex particle isoelectric. Under the experimental conditions which were kept constant for the entire series of measurements, the untreated colloid was found to migrate 7.2 mm., the same sol (0.1%) to 100 cc. of which 2 cc. of 0.01 N HCl had been added, moved 5.75 mm. When the amount of acid added was increased to 4 cc. no migration whatever was obtained and the colloid settled out on prolonged standing,

indicating that ionization of the colloidal acids had been completely repressed.

If on the other hand we were to add a base like NaOH to the acid colloidal clay, we would expect that the Na salts of the acids would be formed:  $(HX)_n + nNaOH = (NaX)_n + nH_2O$ .

Since small quantities of alkali tend to peptize this colloid, to decrease its viscosity and raise its electrolyte requirement we would expect that  $(NaX)_n$  would be more highly dissociated than  $(HX)_n$ . This has been found to be true generally of the salts of strong bases and weak acids. If that were true we would expect such a colloid to migrate more rapidly than the untreated colloid. The migration velocity should reach a maximum when just enough NaOH has been added to convert all of the colloidal acids into the salts. The mass action equations for such a salt might be represented by the equations:

$$\frac{(Na')(X')}{(NaX)_n} = K_1, K_2, \dots K_n.$$

in which  $K_1, K_2, \dots K_n$  represent the dissociation constants of the different single salts making up the complex colloidal particle.

Any excess NaOH over that required for neutralization would then be expected to retard the migration because of the common ion effect. The migration velocity would be expected to be reduced in steps as the concentration of the common ion becomes great enough to completely repress successively (in the order of their strengths) the ionization of the salts whose dissociation constants are represented by  $K_1, K_2, K_3, \dots$  until the concentration was sufficiently great to repress completely the ionization of the most highly dissociated of the group,  $K_n$ , when it would be reduced to zero. Experiments show the following effects due to treatment with NaOH.

0.1% untreated colloid—7.2 mm.

100 cc. 0.1% colloid 2 cc. 0.01 N NaOH—11.5 mm.

“ “ 6 cc. “ “ — 9.0 “

“ “ 10 cc. “ “ — 3.0 “

“ “ 20 cc. “ “ — 0.0 “

(Titration measurements indicate that 3.3 cc. of 0.01 N NaOH were required for neutralization.)

These measurements were made over a year before the other studies reported above and their application to the theory pre-

sented was not realized at the time, consequently they do not cover the different ranges of concentration as closely as they should but in spite of their preliminary character, they substantiate the later studies by indicating the ionic nature of the reactions and the applicability, at least in a qualitative way, of the classical laws of chemistry to the reactions of colloidal clays.

#### CONCLUSIONS

In conclusion let us see if this conception of the true acid character of the colloidal clay of acid soils is adequate to explain the well established facts of soil acidity which were cited above. (1) The natural variation in the H ion concentration of acid soils can be accounted for by the known variation of the colloidal fraction. (2) The fact that the aqueous extracts of acid soils when freed from  $\text{CO}_2$  are acid free would be expected if we were dealing with a colloidal acid, for in preparing aqueous extracts the colloidal material has always been carefully removed. (3) The liberation of free acid from acid soils by neutral salts would be expected if a very weak colloidal acid  $(\text{HX})_n$  were treated with such a salt as KCl. When equilibrium is established a certain amount of the K salt of the weak colloidal acid would be expected to be formed and a corresponding amount of the free acid, HCl, liberated. Because of its more complete dissociation the liberation of very slight traces of HCl would raise the H ion concentration of the unbuffered aqueous extract higher than the normal value of the soil. (4) The fact that the titration curves of soils, as ordinarily made are linear, is shown to be in harmony with the colloidal acid theory. (5) The well established fact that the buffer action of soils is directly proportional to their colloid content, is again exactly what would be expected if their acidity were due to acids of colloidal dimensions. The colloidal acid theory, then, seems to be in harmony with all the well established facts of soil acidity.

Let us reconsider briefly the principal arguments against the true acid theory of soil acidity in light of the colloidal acid conception. (1) The argument of Salter and Morgan that soil acidity is an adsorption phenomenon, because of the fact that in the soil-water ratios studied by them an exponential relation with the H ion concentration was observed, is shown to be unconvincing since in these soils the colloid content was probably

too low to permit the reaching of a concentration of the colloidal acid that would yield a fairly constant hydrogen ion concentration. The relation of the concentration of the colloidal clay acid to its H ion concentration is found to be of a type similar to that of weak crystalloid acids. (2) The fact that the titration curves of soils show no sharp breaks indicative of end-points, is shown to be due to improper experimental procedure. When a strong base is titrated with the weak soil acid, definite end-points are obtained by both the conductivity and H electrode methods. It is also shown that the end-point in the titration of the colloidal acid and a base may be located by flocculation studies, by determining the alkali content of the least alkaline mixture in the constant electrolyte requirement zone. Cathaphoresis studies also locate the end-point at the alkali content producing the maximum migration velocity. Viscosity measurements may also be used, the point of minimum viscosity representing the point at which all the colloidal acid is converted into the more highly dissociated salt. All of these methods are shown to give end-points at approximately the same place. The titration curves of colloidal clay acids seem to be characterized by the diversity of methods of determining the end-point rather than the lack of such end-points. (3) The argument that the reactions are not stoichiometric is likewise shown to be due to improper experimental procedure and failure to take solubilities into consideration. Stoichiometric quantities of NaOH and  $\text{Ca(OH)}_2$  are required to reach the end-point in the titration of the colloidal clay by the flocculation method, the H electrode method and the conductivity method. (4) The argument of Russell that "no one has ever isolated an undeniable acid in quantities commensurate with the soil's sourness" is shown to be untrue if we consider the colloidal acid an "undeniable acid." The mineral acid theory of soil acidity has not been as widely accepted as it seems to deserve, because its advocates were always searching for an acid of crystalloid dimensions and took particular pains in all of their investigations to eliminate all colloidal material. When we consider the great complexity of the soil minerals from which the soil acids must have been derived, it would seem much more logical to expect acids of colloidal dimensions rather than true crystalloids. In fact, silicic acid, the simplest possible acid of this group, while

it can be prepared as a crystalloid, changes rapidly into a colloid on standing.

#### DISCUSSION ON R. BRADFELD'S PAPER

### THE NATURE OF THE CHEMICAL REACTIONS OF COLLOIDAL CLAY

N. E. GORDON: I wish to call your attention to a correction in Mr. Bradfield's paper. He says that he is the first to carry out any work on colloids from a control of hydrogen ion concentration standpoint. As a matter of fact we have been working on this for two or three years and have published our results in *Soil Science* and *Science*, but evidently Dr. Bradfield has not seen these articles. Personally, I do not see that Mr. Bradfield has made any advance whatsoever over what could have been anticipated from the work already done on soil colloids. At the University of Maryland we do not believe that you can work with a system as complex as soil which not only contains at least four distinct colloids, all of which act differently from a chemical standpoint, but in addition to this, many soil salts, and in the end interpret the results from a chemical standpoint. In view of this belief we have begun a study of synthetic soil colloids, beginning with the individual colloids in their purest condition and noting the effects of the individual salts on the respective colloids. By getting the individual results and then by building up our complex soil colloids, introducing the minimum number of new factors at each step, we feel that our final conclusions will be much less speculative than those of Mr. Bradfield's.

R. BRADFELD: I think Dr. Gordon has misunderstood. What I said was with reference to the effect of hydrogen ion concentration upon the flocculation of colloidal clay, and he was speaking about the effect of hydrogen ion concentration upon adsorption by silica gel. I have been working for some time on the effect of hydrogen ion concentration upon the adsorption and liberation of bases by soil colloids. This work was not mentioned in this paper because it has not been completed. The results obtained thus far are in accord with the findings of Dr. Gordon and his pupils and tend to support the theory of the nature of the chemical reactions of colloidal clays presented



above. I am familiar with the papers referred to by Dr. Gordon, in fact I abstracted them for *Chemical Abstracts*. I did not mention these papers because they were not directly related to the point I was discussing. It seems significant, however, that these independent investigations tend to point to the same conclusions.

Great care must be taken, however, in applying results obtained on pure colloidal silica to soil colloids. The soil colloids contain on an average about 50%  $\text{SiO}_2$ , but in all probability only a very small percentage of that  $\text{SiO}_2$  exists as free colloidal silica. The great bulk of it seems to be present in the form of complex aluminosilicates. Comparative studies made in my laboratory<sup>7</sup> of the properties of colloidal clay, colloidal silica and a synthetic colloid having the same total analysis as the natural colloid, show that entirely different systems are involved in each case. Valuable as studies of the properties of pure colloidal silica may be from the standpoint of colloid chemistry, they probably do not furnish an adequate explanation of the reactions of soil colloids. My work on the material extracted from the soil indicates that if the hydrogen ion concentration is controlled the reactions yield definite and characteristic end-points in spite of the complexity of the molecule involved.

N. E. GORDON: That is true; it is all right to work with soils, but I say the proper approach is the other way. We have been working a thousand years on soils and we do not know any more about soils than when we started. How in the world can you learn anything about it when you are working with a thousand theories at once.

R. BRADFIELD: We have not been concerned thus far in our work with the exact structure of the molecules involved in colloidal clay. But we are very much concerned with the nature of the reactions that take place when soils are treated with different acids, bases and salts. I used the "X" as a simple expression for the negative ion and showed that, regardless of the structure of that ion, its reactions seem to follow the ordinary laws of chemistry, and that complex theories are not necessary. I think all soils men will agree that very different ideas of soil acidity are prevalent.

<sup>7</sup> R. Bradfield, *Missouri Agr. Ex. Sta. Research Bull.*, 60 (1923)

H. GROSSMAN: I would like to know whether it is possible to re-suspend the clay material after it has been removed by centrifuging. Also how great is the loss upon ignition of this material?

R. BRADFELD: The loss on ignition is high and the amount of organic material is small. The loss on ignition is not due entirely to organic material but largely to water.

H. GROSSMAN: How about the material thrown down by centrifuging?

R. BRADFELD: I have not made any very thorough studies of the coarse material that is thrown down. It contains considerable quantities of colloidal material. I cannot answer your question because I have never worked with material from which the colloidal fraction has been removed completely.

E. O. KRAEMER: I do not understand Dr. Bradfield's explanation for the change in cataphoresis with increasing concentrations of sodium hydroxide. The suggestion was that the excess sodium hydroxide represses the ionization of the sodium salt of the "clay-acid."

R. BRADFELD: That was the idea represented.

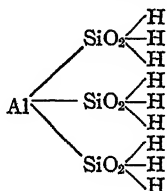
E. O. KRAEMER: What is supposed to be the basicity of this acid?

R. BRADFELD: Some of my curves indicate the possibility that it may be di-basic. Near a  $p_H$  of 7 there is a slight break in the titration curves (made with the hydrogen electrode).

E. O. KRAEMER: The point I should like to raise is this, the change in cataphoresis cannot be continuous if the change is due to repression of ionization, because the particles which are moving under this difference of potential are assumed to be the ions formed by the ionization and they have a definite charge. If a particle loses its charge by reversal of ionization the total number of particles having that charge changes, but as far as the speed or velocity with which these particles move, that remains constant as long as there are any particles having that given charge.

R. BRADFELD: I don't quite get your point. The minerals, for instance, may be considered as built up from different com-

binations of the salts of such a complex acid as



We would expect that each H would have its own dissociation constant.

E. O. KRAEMER: The point is this, however; it is not a question of the number of these ions, if these charged particles are due to a dissociation of the salt of the type which is indicated there. We might even assume that there are a number of different "clay-salts." However, these different kinds of particles could be classified into different groups according to the charges on the particles. The charges on these particles would vary in steps instead of continuously, and therefore the measurement of cataphoresis would indicate discontinuities in the velocities with which these particles move. However, if these velocities vary continuously, I cannot see how the charge of the particles can possibly be due to any such ionization.

R. BRADFELD: The charges may vary in steps but in salts as complex as the ones we are dealing with in colloidal clay the steps are so close together that the rough measurements presented do not reveal them. The data were presented only as a qualitative indication that the reactions followed the mass law. How would you explain the fact that small quantities of NaOH increase the migration velocity, while slightly larger quantities decrease it and finally bring it to zero?

E. O. KRAEMER: I might suggest that the sodium ion and the hydroxide ion may have separate and distinct adsorption isotherms and that these two curves (indicating) may approach or cross each other. In such a case the charge on the particle, and therefore the velocity of cataphoresis, depends upon the difference in adsorption of the two ions. As the adsorption isotherms approach each other, the charge and velocity of cataphoresis continuously decreases.

Moreover, with a sufficient change in the sodium hydroxide concentration there may be a reversal of charge. This there-

fore would account for the perfectly continuous change in the cataphoresis.

R. BRADFELD: I know the explanation is commonly put forth by those who believe in the adsorption theory. But we have here (indicating) definite end-points. You will note that we have five different methods of locating the end-point in these titrations, and they all indicate that we have neutralization at about the same point. We can determine at which point all this colloidal acid is turned into the salt, rather accurately.

Sharp end-points have not been considered characteristic of adsorption phenomena while they are known to be characteristic of chemical reactions.

E. O. KRAEMER: With respect to this last argument, it may be pointed out that a clay particle having a complex aluminosilicate structure as suggested by Dr. Bradfield would be expected to behave as a polar adsorbent. In such a case, adsorption would be of the monomolecular type as used by Langmuir in his theories of adsorption. That is, one might expect end-points of the kind described by Dr. Bradfield. Quasi-end-points are met when  $1/n$  of the adsorption formula  $a = Kp^{1/n}$  has a small value.

F. E. BARTELL: I would like to say that a number of years ago I started exactly this same investigation myself, and ran into most of these difficulties, and finally appreciated the point brought out by Dr. Gordon and chose the purest type of carbon we could prepare. It has taken us a number of years to get anywhere with that.

E. TRUOG: I believe the suggestion of using the pure materials is a good one. Harper found in our laboratory that practically all clays contain a certain amount of ammonia, which can be removed. After it is heated the acidic properties of the clay increase very greatly due to a removal of the ammonia. If it is heated too much its activity as an acid is decreased very considerably. However, when allowed to remain in contact with water it will regain its acidic properties to some extent. We did some work trying to prepare some of these pure acids from pure minerals by treatment with carbonated water and found that the acidic residues which are obtained from the different minerals vary greatly in acidity. I think one good way of obtaining pure acidic materials of the soil is by starting

with the pure crystalline material and leaching them with carbonated water.

Referring to the recent paper of Salter of Ohio (in *Soil Science*), I think there is an important point to consider in the case in which he has treated soils with different amounts of water. He says that the acidity cannot be due to an insoluble acid, because in the presence of an excess of these insoluble acids, the hydrogen ion concentration should but does not remain constant. In the soil, as we start with it, we always have soluble nitrates, sulphates, and chlorides, and the addition of a salt of this kind in moderate amounts always increases the hydrogen ion concentration. Now, as we dilute the solution we decrease the concentration of these soluble salts, and hence we would expect the hydrogen ion concentration to go down, just as he found.

A. L. FERGUSON: I have here an abstract of an article by O. Arrhenius, describing some work carried out in Harvard University under the direction of Prof. Osterhout and published in the *Journal of the American Chemical Society*, Volume 44, page 521 (1922). He states, as a conclusion of his work, "We know that clay acts as an amphoteric electrolyte and can therefore combine with either acids or bases." He draws a rather far reaching conclusion from his work. At the end of the article he makes the following statement: "The facts here shown may have a revolutionary effect on our conception of soil and soil conditions. We may dispense with such convenient words as adsorption, used by the colloid chemists, since we see that purely physical chemical laws find an application to mineral colloids also in the case of soils. That word colloid will then mean only a particle of special dimensions but not of special properties."

I also would like to ask a question with regard to this equilibrium. After neutralization with sodium hydroxide, has an attempt been made to repress the electrolytic dissociation by increasing the sodium ion concentration by adding sodium chloride instead of sodium hydroxide?

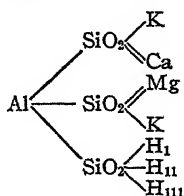
R. BRADFELD: Not in the cataphoresis studies, but the flocculation studies indicate that the sodium chloride would be just as effective as sodium hydroxide after you once add enough of the hydroxide to neutralize the acid of the clay.

A. L. FERGUSON: I was also wondering if any salt has been used other than a salt containing a sodium ion.

R. BRADFELD: I have used a series of calcium chloride-calcium hydroxide mixtures in flocculation studies. The same type of curve is obtained. The only difference is that the amount of calcium required for flocculation is much less than the amount of potassium, but the amount of calcium hydroxide necessary to reach the zone of constant electrolyte requirement is the same as with KOH, indicating that the same amount of acid has to be neutralized before the constancy in the electrolyte requirement is obtained.

H. S. TAYLOR: I think it ought to be pointed out that such an equality does not necessarily imply that you are dealing with a strict chemical reaction. It may imply that there is a small value to the amount of hydroxide ion adsorption. I think it would be very nice if you could prove that you are dealing with a simple chemical reaction. Furthermore, there is something wrong with this particular thing here (indicating), because the velocity of migration as Mr. Kraemer has pointed out is not a function of degree of dissociation. The velocity of migration is independent of the amount of dissociation within quite large limits of concentration.

R. BRADFELD: I agree with Dr. Taylor and Mr. Kraemer that the velocity of migration of a simple ion like Na would be entirely independent of the degree of dissociation. In that case we are dealing with one and the same ion throughout a wide range of concentrations. I am inclined to feel, however, that the situation may be somewhat different when we are dealing with very weak acid salts as complex as the ones we seem to have in colloidal clay. As pointed out above, F. W. Clark has shown that soil minerals may be considered as built up from combinations of such complex aluminosilicates as



We would expect, for instance, that each hydrogen or metal in the combination would have a slightly different dissociation constant, that for example  $\text{H}_1$  would tend to split off as an ion

more readily than  $H_{11}$ ,  $H_{11}$  more readily than  $H_{111}$ , etc. The negative charge on the colloidal particle would certainly increase as the number of positive ions split off increased. Our measurements show that the sodium salt of an acid colloidal clay is a much better conductor of electricity than the original acid. According to our present theory that would tend to indicate that the sodium salt was more highly ionized than the acid. Our cataphoresis measurements show that the addition of sufficient NaOH to convert the acid clay into its sodium salt results in an increase in the migration velocity. As we increase the concentration of the sodium ion by the addition of more NaOH, the ions coming from the colloidal complex are driven back into their place in turn, first  $Na_{111}$ , then  $Na_{11}$  and finally, when the concentration of the NaOH becomes great enough,  $Na_1$ . At this point the ionization becomes zero and consequently movement in an electric field ceases.

This explanation may not be the true one; it certainly needs more experimental confirmation. Additional factors may be operating. All of the other measurements reported above indicate that the reactions of colloidal clay are of the same general type that are encountered in the case of very feebly ionized crystalloids. If this be true we would expect the mass law to hold. I feel that the cataphoresis measurements indicate at least a qualitative agreement with what we would expect if the reaction did follow the mass law.

M. S. ANDERSON: It might be of interest to make a remark with regard to the quantities of this colloidal material present in the soil. At the Bureau of Soils we have extracted as high as 38% of this submicroscopic material from agricultural soils, of course this amount was from a heavy clay soil. We have obtained 10 to 15%, however, from soils of medium texture such as the loams. In no case were we able to separate all of the colloid.

There is another point also of interest in this connection. The distribution of the material does not seem to be exactly in accordance with the theory as expressed. It has seemed from our repeated washing of soil samples that practically all of the colloidal material surrounding mineral grains is relatively easy to wash off. The aggregates of colloid, however, are very difficult to wash off. The aggregates of colloid, however, are very difficult to wash off. The aggregates of colloid, however, are very difficult to wash off.

seen microscopically in the residue together with clean looking mineral particles.

E. TRUOG: I think it is important to note that the amount of basic materials which soils take up is very much greater than in the case of materials like carbon black; in fact soils will take up perhaps a hundred times the amount of bases that these common materials do which have been used in adsorption experiments.



[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIO-CHEMISTRY, UNIVERSITY OF MINNESOTA]

## THE APPLICATION OF COLLOID CHEMISTRY TO SOME AGRICULTURAL PROBLEMS

BY ROSS AIKEN GORTNER

Agriculture is the basic industry of the world. All of the activities of mankind can, in the last analysis, be translated into the bushels of grain, and pounds of meat which are necessary to supply his energy. More than one hundred years ago Malthus in his "Essay on the Principle of Population" stated that, "The power of (increase in) population is indefinitely greater than the power of the earth to produce subsistence for man." Pearl<sup>1</sup> has recently had occasion to reëxamine the problem which troubled Malthus and states, "It will appear with startling emphasis that nothing which has happened since 1798 has in the least degree mitigated or softened or altered in any true sense the relentless insistence of Malthus' logic. On the contrary, the developments of the last century have made it far plainer even than it was to so clear visioned a major prophet as he was, that the population of the world cannot go on increasing at anything like the rate of growth that has prevailed in the past more than a short time longer." East<sup>2</sup> points out that the normal increase in population of the world calls for an additional thirty-seven million acres each year to be brought under the plow. Much of the desirable agricultural land is already under cultivation; in the near future we must utilize more and more of the undesirable land if the world does not go hungry. As a biological friend of mine recently remarked, "If our grandchildren do not face this problem, their grandchildren certainly will."

Taking therefore the thesis that agriculture is the basic industry of the world because it produces the food of man, and adding to this the thought that within at the most a few short centuries the food available will limit population, it behooves us to take stock of our supply of knowledge and see if we can find new tools which may be enlisted in the service of agriculture.

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<sup>1</sup> Pearl, R., "The Population Problem," *Geog. Rev.*, **12**, 636-645 (1922)

<sup>2</sup> East, E. M. "Future Food Prospects," *World Agriculture*, **2**, 130-32 (1921)

It is my firm conviction that the most potent tool lies in the application of our knowledge of the colloidal state to problems of agriculture.

Agricultural chemistry in America is largely the outgrowth of the development of our Agricultural Colleges and Experiment Stations. In many instances the work in agricultural chemistry has been sharply delineated from that in so-called "pure" chemistry in that the agricultural chemist is supposed to attack only economic problems which appear capable of solution. This requirement has no doubt in many instances prevented a solution of the problem, for the theoretical basis which must precede the practical application was unknown or imperfectly understood.

On the other hand, the so-called "pure" chemist may be even more incapable of applying his theoretical knowledge to agricultural problems, for, while he knows the theory he may not recognize or understand the problems which arise in actual practice, or he may not recognize the barriers which limit the application of laboratory knowledge to agricultural practice. The agricultural chemist should be more than a chemist; he should have a rather broad knowledge of the fields of animal biology and botany, a rather detailed knowledge of cell structure and function, and above all an absorbing interest in every phenomenon which is or may be involved in living processes, for in the last analysis agricultural chemistry is more truly biological chemistry than is the pathological chemistry, often misnamed biological chemistry, of the curricula of our medical schools.

The applications of colloid chemistry to agriculture are the applications of colloid chemistry to living processes. The cell may be thought of as a complex of proteins, fats, carbohydrates, salts, and water. Bechhold<sup>3</sup> has calculated that the average liver cell contains:

225,000	billion	molecules	of	water
53	"	"	"	protein (M. W. = 16,000)
166	"	"	"	fat and lipoids (M. W. = 166)
2900	"	"	"	crystalloids (M. W. = 100)

The protein is certainly in the colloidal state; the fats and lipoids exist largely in the form of emulsions, which may be

<sup>3</sup> "Colloids in Biology and Medicine," Van Nostrand Company, 1919, p. 276

regarded as obeying essentially the laws of the colloidal state. But what of the crystalloids and the water? Undoubtedly a very considerable part of the mineral salts are combined with or adsorbed upon the colloidal particles. To what extent this holds true is as yet problematical. But what has not been recognized as widely as it should be is that *the water may exist very largely in the colloidal state*, that is, it may exist as water of imbibition.

I have recently pointed out<sup>4</sup> that proteins may exist in molecular solution and still be in the colloidal state due to the fact that the water of imbibition swells the protein molecule so as to bring it well within the limits of size which determine the colloidal realm and that such "bound" water must be differentiated from "free" water. In other words, we may have two plants the tissues of which may contain exactly the same amount of dry matter and yet have entirely different physiological processes going on in the two plants due to a difference in "bound" water content. It has been demonstrated that enzyme reactions are equilibria, that emulsin hydrolyzes glucosides in dilute solutions and resynthesizes glucosides in concentrated solutions, and it appears highly probable to me that the direction of enzyme action, whether hydrolytic or synthetic, taking place in the living cell is regulated, at least in a large measure, by the ratio of bound water to free water. If this be true it becomes apparent that methods for estimating bound water in biological tissues and fluids are most desirable.

One such method has recently been proposed the application of which has already yielded notable results. Newton and Gortner<sup>5</sup> recommend the following method when working with biological fluids.

The depression of the freezing point,  $\Delta$ , of the fluid is first obtained. A moisture determination is then made by any convenient method<sup>6</sup> and to a weighed portion of the fluid enough sucrose is added to make exactly a molar solution in the total water which is present. A new freezing point depression,

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<sup>4</sup> Sharp, P. F., and Gortner, R. A., "The Physico-chemical Properties of Strong and Weak Flours, V," *Journal of Physical Chemistry* (in press)

<sup>5</sup> Newton, R., and Gortner, R. A., "A Method for Estimating Hydrophilic Colloid Content of Expressed Plant Tissue Fluids," *Botanical Gazette*, **74**, 442-446 (1922)

<sup>6</sup> When working with plant saps the refractometer method of Gortner, R. A., and Newton, R., *Botanical Gazette*, **74**, 202-212 (1922) is eminently satisfactory

$\Delta a$ , is then taken. If no hydrophilic colloids are present this second freezing point will be  $2.085^\circ$ <sup>7</sup> lower than  $\Delta$ . If on the other hand hydrophilic colloids are present there should be an excess depression over the expected  $2.085^\circ$  due to the fact that some of the water is "bound" by the hydrophilic colloids and is not free to dissolve cane sugar, thus causing a sugar solution more concentrated than normal to be formed. The

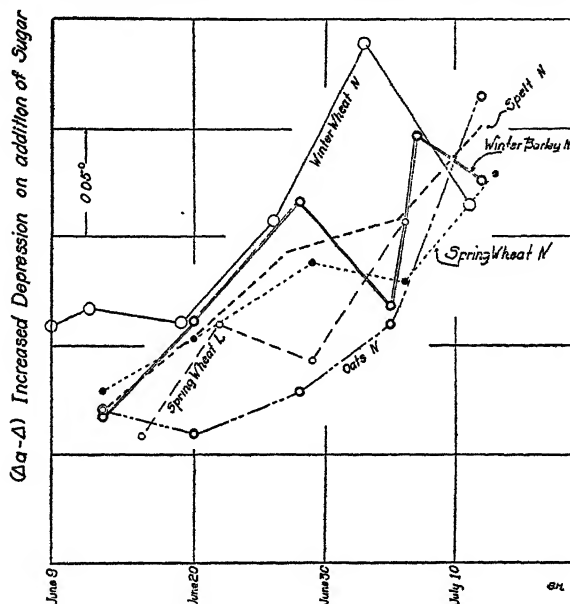


Figure 1.—Increase with the season of bound water in cereal saps growing under dry farming conditions.

minimum amount of bound water may be calculated by a simple formula:

$$\frac{\Delta a - (\Delta + Km)}{\Delta a - \Delta} \times 892 = \text{grams bound water per liter of solvent.}$$

This method has already been applied to two agricultural problems. Dr. J. Arthur Harris and co-workers have used it in connection with other physico-chemical methods on a series of cereal saps grown in Utah under dry farm conditions. Figure 1

<sup>7</sup> This is the molecular constant,  $K_m$ , for sucrose due to the fact that sucrose forms a hexahydrate in solution. Cf. Scatchard, G., "The Hydration of Sucrose in Water Solution as Calculated from Vapor Pressure Measurements," *J. Am. Chem. Soc.*, **43**, 2406-2418 (1921)

is a graphic representation<sup>8</sup> of the increase in bound water with the progress of the season. In this same series it was observed that there was a marked increase in osmotic pressure of the plant sap as the season progressed. We have thus two factors, *i. e.*, osmotic and hydrophilic colloids, which work together to (a) draw moisture from a dry-out soil and (b) to hold moisture in the cell against transpiration. The literature dealing with the magnitude of the osmotic forces is rather extensive and shows that these may reach exceedingly high values. Harris, Gortner, Hoffman, and Valentine<sup>9</sup> report a depression of the freezing point of 14.4° equivalent to 169 atmospheres osmotic pressure in the sap of *Atriplex Nuttallii*, a typical halophyte growing near the southern shore of Great Salt Lake. In this form it is probable that osmotic forces play the major rôle. On the other hand certain extreme xerophytes, notably the cacti, are remarkable for the extremely low osmotic concentration of the cell sap. In many instances the osmotic forces as measured by depression of the freezing point do not exceed 10 atmospheres and are less than those found in the herbaceous vegetation of our mesophytic regions. It is in such forms that the hydrophilic colloids play their maximum rôle, and the resistance which these forms show to desiccation is undoubtedly due to the fact that the water is "bound" by the colloids. Figure 2 shows a cactus, *Opuntia Sp.*, growing in three inches of soil on the roof of an adobe house near Tucson, Arizona. The ability to resist desiccation under such conditions when exposed to an Arizona summer shows the remarkable water-retaining capacity of the colloids present in the plant. My attention was recently called to another example illustrating this point. Joints of *Opuntia inermis* were placed in a museum case in the Botany Building of the University of Sydney, Australia, in 1919 and were found to be growing in

<sup>8</sup> I wish to express my thanks to Dr. Harris and the officials of the Bureau of Plant Industry, U. S. Department of Agriculture, for permission to use these data in advance of their own publication. The individual points on the graph represent average values of all varieties tested. The wheat curves contain sufficient determinations to make them fairly trustworthy. In some instances as many as 23 determinations have been averaged for a single point. The data for oats (averages of triplicates), barley (duplicates) and emmer (individual determination) must be regarded as merely indicative of the form of the curves.

<sup>9</sup> Harris, J. Arthur, Gortner, R. A., Hoffman, W. F., and Valentine, A. F., "Maximum Values of Osmotic Concentration in Plant Tissue Fluids," *Proc. Soc. Exp. Biol. Med.* 18. 106-9 (1921)

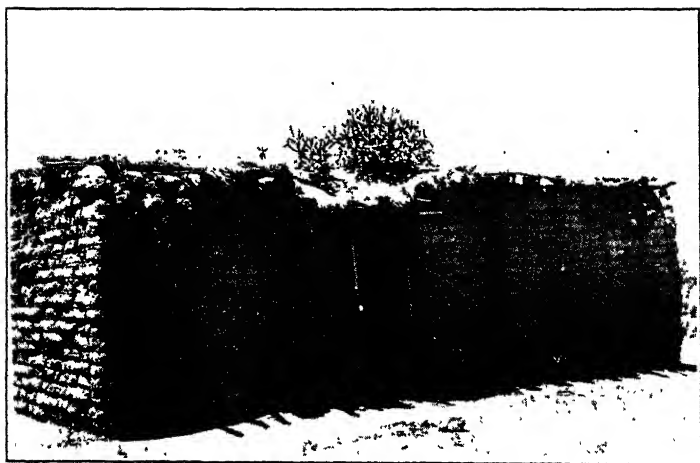


Figure 2.—*Opuntia* *Sp.* growing in 3 inches of soil on the roof of an adobe house, Tucson, Arizona. Annual rainfall about 10 inches.



February, 1923. That is, the moisture and stored foods were being transferred from the old joints and new growing joints were forming.

The above examples indicate strongly that if we are to make agricultural use of our arid and semi-arid areas the question as to whether or not a plant has the ability to elaborate hydrophilic colloids in its cells may be the determining factor as to whether or not that plant can yield a crop in the region in question. Plant breeders are breeding for drouth resistance and are spending large sums on field experiments testing out new sorts, hybrids, etc. It is my belief that a laboratory test for drouth resistance is well within the realm of possibility, such a test to be based upon water-retaining capacity due to the presence of hydrophilic colloids.

One of the most striking examples of the relation of colloids to the problems of Agriculture is found in the problem of the production of winter-hardy plants. This is a question which is of extreme importance in regions as far north as Minnesota and the plant breeders of our experiment stations have been attempting to develop new varieties which will not winter kill under conditions of our northern winter. Mr. Robert Newton has been working in our laboratories for the past three years upon the problems of the fundamental chemistry of winter-hardiness in wheat. He finds<sup>10,11</sup> that it is again a question of the elaboration of hydrophilic colloids. Ordinarily wheat leaves are very readily frozen and after freezing and thawing it is possible to press 50 to 65 cc. of sap from 100 grams of leaf tissue. If, however, plants of a winter-hardy variety of wheat cool down slowly to below the freezing temperature, under conditions such as prevail in a field plot, so that they become slowly "hardened off" it is no longer possible to "kill" such leaf tissue even by extremely low temperatures so as to extract sap from the leaves by pressure. Samples of such "winter-hardened" leaves have been subjected to a low temperature produced by calcium chloride and snow mixed in the proportions to give a cryohydrate mixture with a corresponding temperature of  $-54.9^{\circ}\text{C}.$ , and on subsequently thawing have, under

<sup>10</sup> Newton, R., "A Comparative Study of Wheat Varieties with Special Reference to Winter Killing," *Jour. Agr. Science*, **12**, 1-19 (1922)

<sup>11</sup> Newton, R., "The Nature and Practical Measurement of Cold Resistance in Winter Wheat." Thesis for Ph.D. degree, Minnesota, 1923



a pressure of 600 atmospheres in a hydraulic press, yielded only 2 or 3 cc. of sap. As a matter of fact winter-hardiness in cereals can best be measured by experiments of this type.

Figure 3<sup>12</sup> shows graphically the quantity of sap which was obtained from six varieties of wheat at different pressures. The order of the curves corresponds exactly to the known resistance of these varieties to winter-killing, Minhardi being most resistant and Fulcaster least resistant to injury by cold. These samples of leaves were collected from field plots on January 21, 1922. Unfortunately the winter of 1921-22 was not

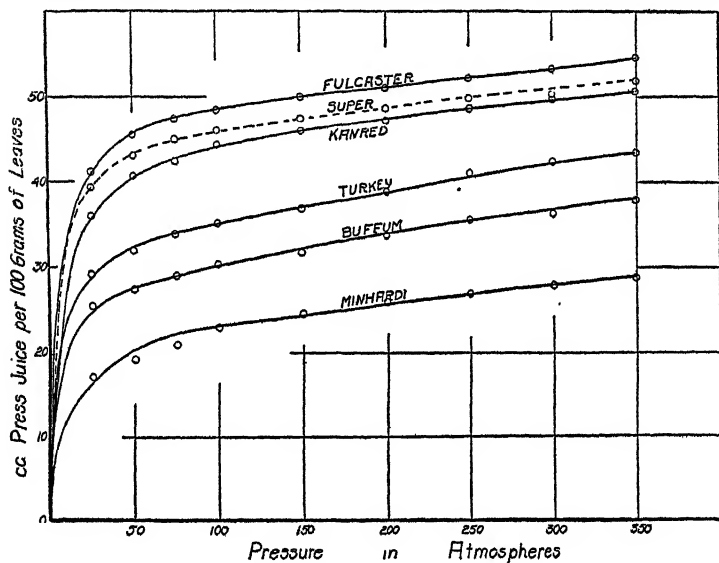


Figure 3.—Pressure dehydration curves of winter hardened wheat leaves. Collection made from field plots, January 21, 1922.

ideal for experimental work of this sort. A heavy snow fell before the ground froze and the soil, saturated with moisture and protected by the snow, remained unfrozen until some time in December. The plants were protected by a snow covering throughout the winter and for this reason did not "harden" to the same degree as in the preceding or the following years. The phenomenal retention of sap in the leaves subjected to pressure was first observed in the winter of 1920-21, but unfortunately an entire series of plots varying in winter-hardiness

was not available. In the winter of 1922-23 at Edmonton, Alberta, Newton reports that he was unable to obtain more than 1.8 cc. of sap when 100 grams of "hardened" Minhardi leaf tissue were subjected to a pressure of 600 atmospheres.

There is no doubt but that the resistance against winter-killing and the retention of water in the tissues against pressure is due to the elaboration of hydrophilic colloids. The viscosity, the gold number, the total solid content, the non-dialysable material, the ratio of total solids to depression of the freezing point, and the average molecular weight of the solutes in the expressed sap, all confirm this conclusion. We have in this instance found laboratory methods which will determine whether or not a given variety of wheat will be winter-hardy. In field plot experiments a "test winter" does not occur every year whereas with controlled temperature in green houses a laboratory test for winter-hardiness could be made subsequent to harvest and prior to seeding time so that in breeding for winter-hardiness at least the tender varieties could be detected and discarded without the necessity of ever planting them in field plots.

The above illustrations may be regarded as typical of the agricultural problems involving plant growth as related to colloid phenomena. Let us turn now to one of the most widely used of the agricultural products, namely wheat and wheat flour. Problems along this line are among the major problems which for many years have interested workers in our laboratories at Minnesota, but it has only been relatively recently that the problems have been attacked from the colloid angle.

As I have already indicated, living and actively growing tissue is primarily dependent upon the colloidal state of the cells, thus, we may regard the development of the wheat berry as involving changes in colloidal state. In the "milk" stage we have a typical colloidal sol and as carbohydrates and proteins are laid down in the berry this sol changes gradually into an extremely viscous gel. In the early stages of development a considerable proportion of the carbohydrates exist as soluble sugars, and a considerable part of the nitrogen exists in non-protein form.<sup>13</sup> These are later synthesized into starch and

<sup>13</sup> Thatcher, R. W., "The Progressive Development of the Wheat Kernel," *Jour. Am. Soc. Agronomy*, 7, 273-282 (1915)

protein, so that extremely small amounts of sugars and non-protein nitrogen remain in the fully ripened berry. It is more than probable that this synthetic action is brought about by the changes from a relatively non-viscous sol to the extremely dense gel.

Bailey<sup>14,15</sup> has shown that the keeping quality of stored grain is dependent upon the amount of moisture in the grain as stored. Figure 4 shows the relation of respiration<sup>16</sup> to

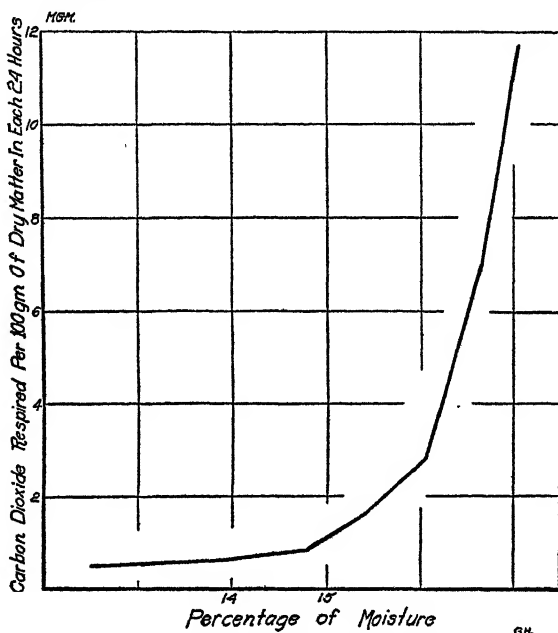


Figure 4.—Respiration (heating) curve of wheat in relation to moisture content of grain.

percentage of moisture in the kernels. It will be noted that there is a sharp increase in rate of respiration when 14.5 per cent. of moisture in the kernel is exceeded. Bailey suggests a logical colloid explanation for the phenomenon. He states,

<sup>14</sup> Bailey, C. H., "The Handling and Storage of Spring Wheat," *J. Am. Soc. Agronomy*, 9, 275-281 (1917)

<sup>15</sup> Bailey, C. H., "The Respiration of Stored Wheat," *J. Agr. Research*, 12, 685-713 (1918)

<sup>16</sup> Rapid respiration means rapid heating of the grain; slow respiration means that the grain will not heat in storage

"Moisture in grain may, in the light of recent discoveries in the field of physical chemistry, be assumed to exist as imbibed water in loose combination with the organic colloids. The organic colloids which form the principal constituents of the wheat kernel have the property of imbibing considerable quantities of water and forming elastic gels. The gel swells as the water is increased, although the total volume of the dry colloid plus the added water is diminished. The water-imbibing capacity of the several colloids varies widely, starch having an imbibing capacity materially lower than that of wheat gluten. There is no fixed amount which a given dry colloid will imbibe; thus, gels of varying viscosity can be produced, depending upon the proportion of water present, and other variables, such as temperature, mineral salts, and other substances. The rate of diffusion in a gel varies with the viscosity. In dilute gels diffusion takes place as in water, while in strong gels the rate is slower. It is probable that in very dry grain the imbibed water is not sufficient to produce a gel in the endosperm structures. The colloidal material there located accordingly does not have a continuous structure, and the possibilities of diffusion are decidedly reduced under such conditions. The exact percentage of moisture below which this discontinuous structure exists in a normal wheat kernel is not known; it probably varies with the percentage of gluten in the grain since gluten possesses a greater water-imbibing capacity than starch. Increasing the moisture content above the maximum at which discontinuity exists results in the formation of a gel through which diffusion can occur. Further increases in moisture content up to maximum imbibition produce progressively less viscous gels, and correspondingly increase the possible rate of diffusion. Since the rate of respiration in grain doubtless depends in part upon the rate of diffusion between the various kernel structures, it follows that the less viscous the gelatinous material of which the cell contents are composed, the more rapid the production of heat through respiration. To restate, the production of heat is dependent upon the activity of the oxidizing enzymes of the kernel, the complex phenomenon being known as respiration. The latter is accelerated by an increase in the rate of diffusion, which in turn is dependent upon the existence of a gel, and the relative viscosity of that gel.

For these reasons the moisture-content of sound grain determines to a considerable extent the rate of respiration and consequent liability of heating when bulk grain is stored." Bailey has adduced additional evidence that respiration is dependent upon gel viscosity. In working with corn<sup>17</sup> he has shown that when the data for CO<sub>2</sub> respired and the electrolytic resistance of the kernel are plotted against moisture-content of the kernels the curves which are obtained parallel each other and that at a low moisture-content there is an enormous resistance to the passage of an electric current. In the case of corn the curves break at about 13 per cent. moisture below which point a vitreous or discontinuous gel is postulated.

In the production of wheat flour several colloid phenomena are involved. To produce a high yield of flour the endosperm should contain an optimum amount of moisture so that the gel of gluten and starch will break sharply when crushed between the rolls. Moisture in excess of this amount occasions a reduction in friability, and thus causes difficulty in milling and a loss of flour into the bran and shorts-streams. The tempering process, which consists in adding water to the wheat a few hours before milling, is designed to hydrate the colloids of the pericarp in order to render the bran tough and elastic so that it will not break to a powder upon the rolls. The length of the tempering process is regulated so as to thoroughly hydrate the pericarp but not to hydrate the starchy endosperm. Thus a wheat may be tempered to a moisture-content of 15 per cent. and yield more flour (with less effort) than will the same wheat at a natural moisture-content of 15 per cent. In the former case we have an unequal distribution of moisture among the wheat colloids which is advantageous to the milling process.

In the attempt to prepare bread from wheat flour we meet colloid phenomena at every turn and I personally believe that within a few years no large bake shop will consider its staff complete unless there is included a chemist trained in the fundamentals of colloids as they apply to biology. The absorption of the water by the flour to form the dough is colloidal adsorption, imbibition. Daniels, Kepner, and Murdick<sup>18</sup> have

<sup>17</sup> Bailey, C. H., "Respiration of Stored Corn," *Tech. Bull.* No. 3, Minn. Agr. Experiment Station, pp. 44 (1921)

<sup>18</sup> Daniels, F., Kepner, B. H., and Murdick, P. P., "The Heat of Hydration and

determined the heat of hydration of wheat flour and report values ranging from 3.01 to 5.78 calories per gram, depending upon the grade of the flour, the percentage of protein and the hygroscopic moisture already present. They point out that heat of hydration may raise the temperature of the dough above the initial temperature of the flour and water which were used.

The intermingling of the proteins, gliadin and glutenin, to form the gluten is undoubtedly a colloidal phenomenon. The retention of the carbon dioxide by the dough in "raising" is governed by the tenacity with which the colloidal particles of the gluten gel adhere to each other. The baking process is in part the transformation of a highly hydrophilic colloid into a denatured protein, much less hydrophilic; and the staling of bread is not necessarily due to a loss of water from the loaf but more often to changes in the hydrophilic properties of the colloids. Syneresis and mould growth are intimately related; in fact the evolution of a loaf of bread presents sufficient colloid problems to satisfy even the most indefatigable worker. Dealing as we are with a biological material we find that no two samples of flour react alike, that new problems constantly arise, and that with our present state of knowledge regarding the colloidal behavior of proteins and gel structure we must apply our efforts to the solution of certain basic principles before we can hope to solve all of the technical problems of bread manufacture.

All wheat varieties are not equally adapted to the manufacture of good bread-flours. Unfortunately the wheat variety is not the sole determining factor in the manufacture of high grade flours, but the climatic and soil conditions under which the wheat is grown are reflected in the quality of the flour which can be milled from that wheat.

The agricultural lands capable of producing wheats yielding flour of high baking quality are of rather limited area and have mostly been brought under cultivation. Flour milled from wheat grown in less favorable regions presents serious difficulties to the baker who endeavors to produce yeast-leavened bread. In certain sections of the world, unleavened bread or hot breads are almost universally used. This is not necessarily a result of a preference on the part of the consumer but rather reflects the undesirable character of the flour used in that region for

the manufacture of yeast-leavened bread. The question as to how such flours can be best utilized in the manufacture of yeast-leavened bread is a question which involves primarily colloid chemistry.

Wood<sup>19</sup> was probably the first to call attention to the possibility that the baking qualities of a flour might be determined at least in part by the physical properties of the gluten. This paper was followed by further work by Wood,<sup>20</sup> and Wood and Hardy<sup>21,22</sup> and these in turn by the work of Upson and Calvin,<sup>23,24</sup> and Ostwald,<sup>25</sup> Lüers and Ostwald,<sup>26</sup> and Lüers.<sup>27</sup> While in all of these papers the colloidal nature of the gluten was recognized, the different degrees of elasticity and tenacity exhibited by the various glutes were attributed to the influence of the acids and salts present in the flour upon the emulsoid colloids comprising the glutes. In other words the viewpoint was taken that the initial state of the emulsoid gel in all flours is essentially the same but that, owing to varying salt-content and the Hofmeister effect of the anions and cations of the acids and salts, the cohesive properties of the gel are affected.

An analysis of the data presented in support of the above hypothesis did not appear to preclude the possibility that the structure of the colloid gels in strong and weak flours might be different. This problem has therefore been attacked in our laboratories at Minnesota. We have shown<sup>28,29</sup> that in

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<sup>19</sup> Wood, T. B., "The Chemistry of Strength of Wheat Flour. I." "The Size of the Loaf," *J. Agr. Sci.*, **2**, 139-160 (1907)

<sup>20</sup> Wood, T. B., "The Chemistry of Strength of Wheat Flour. II." "The Shape of the Loaf," *J. Agr. Sci.*, **2**, 267-277 (1917)

<sup>21</sup> Wood, T. B., and Hardy, W. B., "Electrolytes and Colloids." "The Physical State of Gluten," *Proc. Roy. Soc. (London)*, **81B**, 38-43 (1908)

<sup>22</sup> Wood, T. B., and Hardy, W. B., "Elektrolyte und Kolloide, Der physikalische Zustand des Glutens," *Koll.-Z.*, **4**, 213-214 (1909)

<sup>23</sup> Upson, F. W., and Calvin, J. W., "On the Colloidal Swelling of Wheat Gluten," *J. Am. Chem. Soc.*, **37**, 1295-1304 (1915)

<sup>24</sup> Upson, F. W., and Calvin, J. W., "The Colloidal Swelling of Wheat Gluten in Relation to Milling and Baking," *Nebr. Agr. Exp. Sta., Research Bull.* **8**, 26 pp., 5 figs. (1916)

<sup>25</sup> Ostwald, Wo., "Beiträge zur Kolloidchemie des Brotes. I." *Koll.-Z.*, **25**, 26-45 (1919)

<sup>26</sup> Lüers, H. u. Ostwald, Wo., "Beiträge zur Kolloidchemie des Brotes. II," *Koll.-Z.*, **25**, 82-90, 116-136 (1919); IV, *ibid.*, **26**, 66-67 (1920); V, *ibid.*, **27**, 34-37 (1920)

<sup>27</sup> Lüers, H., "Beiträge zur Kolloidchemie des Brotes, III," *Koll.-Z.*, **25**, 177-196, 230-240 (1919)

<sup>28</sup> Gortner, R. A., and Doherty, E. H., "Hydration Capacity of Gluten from Strong and Weak Flours," *J. Agr. Research*, **13**, 389-418 (1918)

<sup>29</sup> Sharp, P. F., and Gortner, R. A., "Physico-chemical Properties of Strong and Weak Flours, II," *J. Phys. Chem.*, **26**, 101-136 (1922)

all probability the quality of the gluten is determined by the colloidal condition of the gluten gel and that this colloidal condition is not dependent upon the acid and salt content of the flour or of the dough but is dependent upon the past history

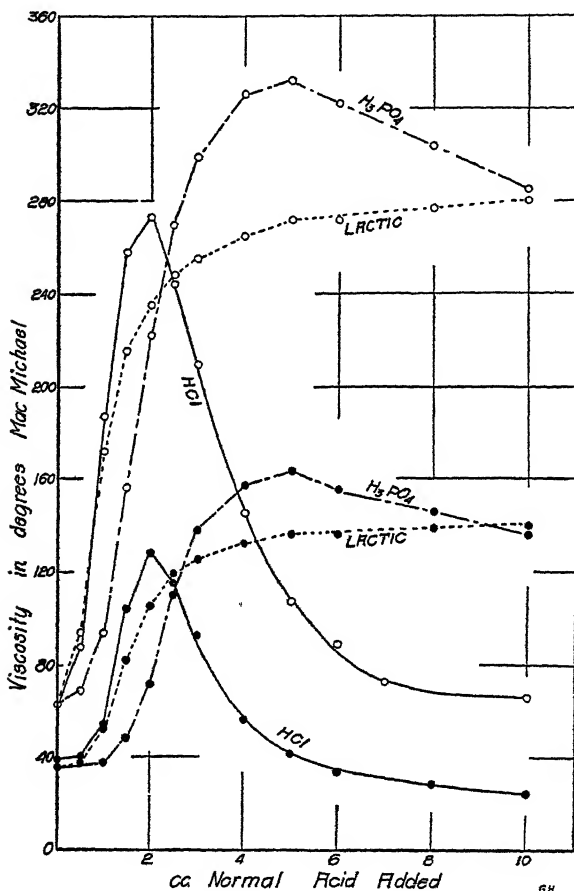


Figure 5.—Imbibition curves of a strong (open circles) and a weak (solid dots) flour with various acids.

of the gluten gel as laid down under conditions of growth in the endosperm of the wheat berry. We have here apparently an excellent example of hysteresis, the "memory" which is associated with emulsoid colloids. In a continuation of this



work we have found that viscosity measurements afford a rapid and accurate means of measuring hydration capacity.<sup>30</sup> Figure 5 illustrates typical imbibition curves which were obtained with strong and weak flours. In Figure 6 these curves are plotted against hydrogen ion concentration of the flour-acid suspension instead of against quantity of added acid. It will be noted that

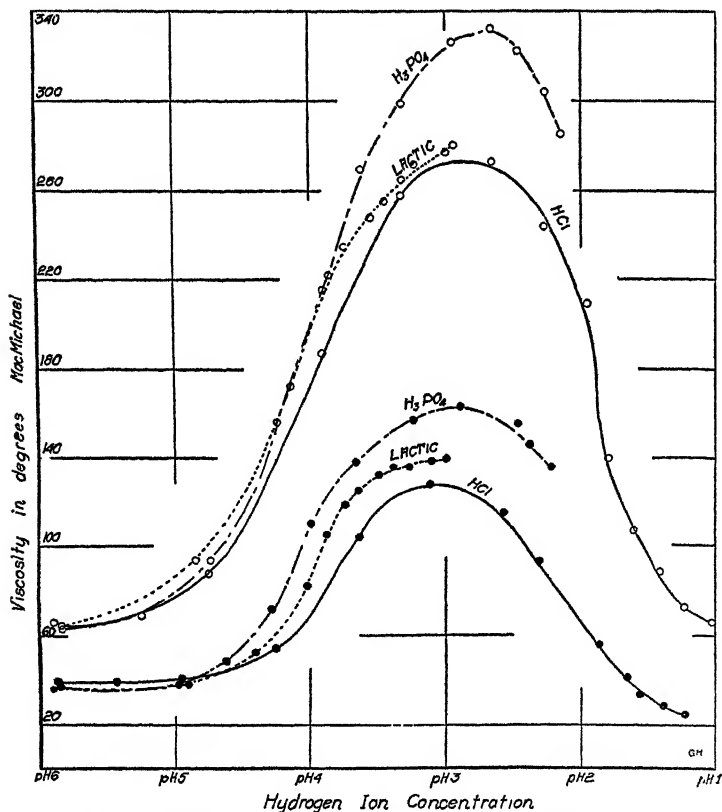


Figure 6.—The same data as in Figure 5 plotted against  $p_H$ .

maximum imbibition occurs at approximately a  $p_H$  of 3.0 in both strong and weak flours. The influence upon hydration capacity of the salts normally present in flour was investi-

<sup>30</sup> Gortner, R. A., and Sharp, P. F., "Physico-chemical Properties of Strong and Weak Flours, III," *J. Phys. Chem.*, 27, 481-492, 1923

gated,<sup>31</sup> and it was found that while the removal of the ash by leaching increased the maximum viscosity it did not affect the observation that strong flours show a much greater imbi-

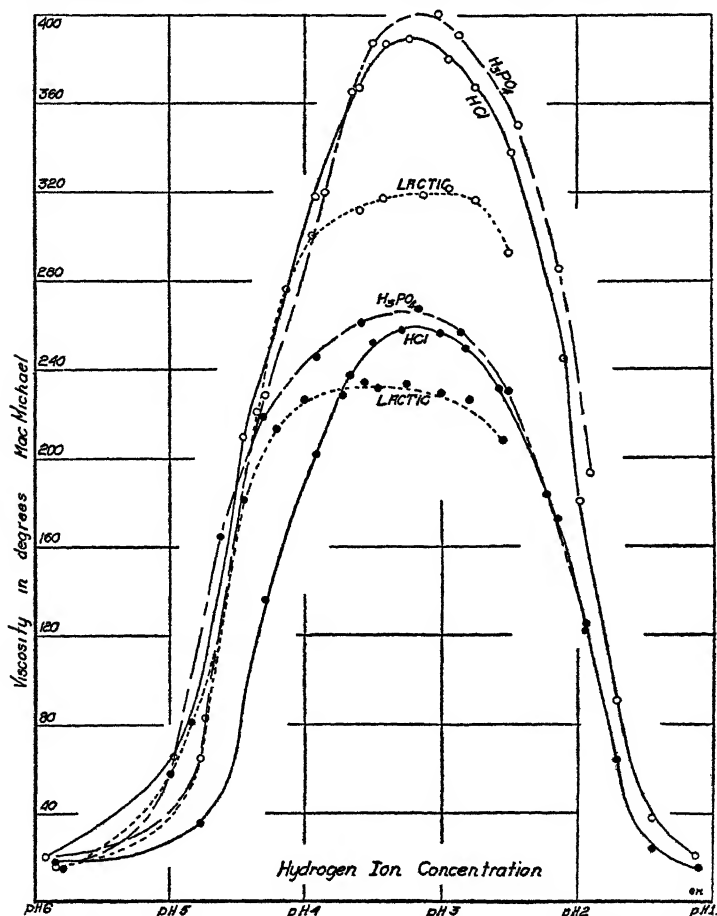


Figure 7.—The same flours as in Figures 5 and 6 but with the mineral salts washed out prior to adding acids.

tional capacity than do weak flours, nor was the maximum point of imbibition shifted from approximately a  $p_H$  of 3.0. Figure 7 shows graphically the results which were obtained.

<sup>31</sup> Gortner, R. A., and Sharp, P. F., "Physico-chemical Properties of Strong and Weak Flours, IV," *J. Phys. Chem.*, **27**, 567-576 (1923)

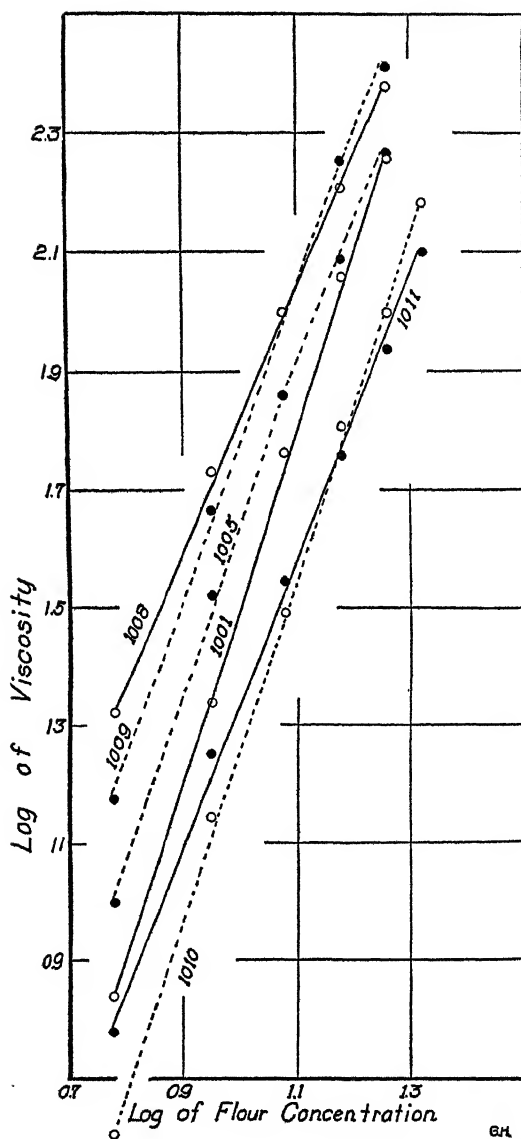


Figure 8.—The relation of maximum viscosity attained with lactic acid to concentration of flour in the mixture.

Additional work<sup>32</sup> indicates that the physico-chemical properties of the gliadin from strong and weak flours are identical and that the colloidal condition of the glutenin is responsible for the different imbibitional capacities. It was found that when the logarithms of the maximum viscosity, attained on the addition of lactic acid to a flour suspension, from which soluble salts had been previously removed by leaching, were plotted against the logarithms of flour concentration the points fell upon a straight line. Figure 8 illustrates such a series of determinations. The equation for such a curve is

$$\log \text{ viscosity} = a + b \log \text{ concentration}$$

where  $a$  and  $b$  are constants.  $a$  is the log of viscosity when the log of concentration is zero and  $b$  is the tangent of the angle made by the logarithmic curve with the axis of abscissa, and serves as a numerical value for flour strength in so far as gluten quality is concerned.

This can be seen from the following consideration. If the logarithmic curve paralleled the axis of abscissa we would have infinite viscosity at minimum concentration, *i. e.*, a super-rubber, on the other hand if it paralleled the axis of ordinates we would have minimum viscosity at infinite concentration, no colloidal properties being apparent.

We have in the past been dependent upon the judgment of the baker or of the cereal chemist as to the quality of the gluten, but we believe that by using methods of colloid chemistry, we can eliminate the personal factor and secure a numerical value to express quality. This will aid not only the miller and the baker in their technical control but also the plant breeder in the problem of producing new and better varieties of wheat.

Another almost virgin field for colloid research lies in Dairy Chemistry and the manufacture of dairy products. It is almost incredible that we do not know the scientific principles which underlie the conversion of cream into butter. The physical chemistry of churning is an almost unexplored field. Fischer and Hooker<sup>33</sup> have suggested that churning is the breaking over of an oil-in-water emulsion into a water-in-oil emulsion, but experimental proof of this hypothesis has not

<sup>32</sup> Sharp, P. F., and Gortner, R. A., "Physico-chemical Properties of Strong and Weak Flours, V, VI, and VII," *J. Phys. Chem.*, 27 (in press)

<sup>33</sup> Fischer, M. H., and Hooker, M. O., "Fats and Fatty Degeneration," *N. Y.*, 1917, pp. 93-4

been available. The following table calculated from data given by Storch<sup>34</sup> shows that the water droplets in butter are very numerous and are highly dispersed.

	Range in diam., mm.	Range in number per cu. mm.
Fat droplets in cream	0.010 to 0.0016	15 to 25 million
Water droplets in butter	0.047 to 0.0011	3 to 13 million

Palmer<sup>35</sup> has had occasion to test the hypothesis of Fischer and Hooker using the method suggested by Bhatnagar<sup>36</sup> for experimental work with emulsions.

An experimental churn was fitted with large platinum electrodes coated with platinum black. Cream was placed in the churn and the churn immersed in a thermostat and held at a constant temperature. As soon as a uniform temperature had been reached the churn paddles were started and kept in motion by a motor and the electrical conductivity followed by means of the conventional Wheatstone bridge set up, alternating current being furnished from a constant speed, high frequency (1000 cycles) generator. Figure 9 shows a typical experiment. It will be noted that the resistance gradually increased as time of churning progressed until it reached a high point "A" and that it then remained practically stationary for 30 minutes ("A" to "B"), the butter begins to "gather," water is squeezed out, and the resistivity falls to the conductivity of the butter milk. A considerable number of experiments gave the same form of curve and tend to support the hypothesis of Fischer and Hooker.

The above examples have been selected from widely varying fields and serve merely to indicate a few selected problems where colloid chemistry has an application to agriculture. Needless to say there are hundreds of problems still unsolved which are probably capable of solution by similar methods.

I have not mentioned the vast field of Soils because, at our Experiment Station, work in soils does not fall in the Division

<sup>34</sup> Storch, V., "Undersogelser over: Nogle ret hyppig forekommende Konsistensfejl hos Smørret og Aarsagerne til deres Fremkomst, samt over: Mælkekuglernes Bygning," *Ses og tredvite Bertning fra den Kgl. Veterinaer-og Landbohøjskoles Laboratorium for landøkonomiske Forsøg*, Copenhagen, 1897

<sup>35</sup> Palmer, L. S., "The Physical Chemistry of Churning," Unpublished data, Minnesota Agricultural Experiment Station.

<sup>36</sup> Bhatnagar, S. S., "Studies in Emulsions," Part I, "A New Method of Determining the Inversion of Phases," *J. Chem. Soc. (London)*, 117, 542-552 (1920)

of Agricultural Biochemistry, there being a separate Division of Soils. The colloid chemistry of soils has interested many workers, but only a few of the many problems which are apparent have been touched upon. Soil acidity in its various aspects could well occupy an army of colloid workers.

When the population of the world begins to become limited by agricultural production the nations will turn their attention to the arable lands of the tropics where three or four crops can

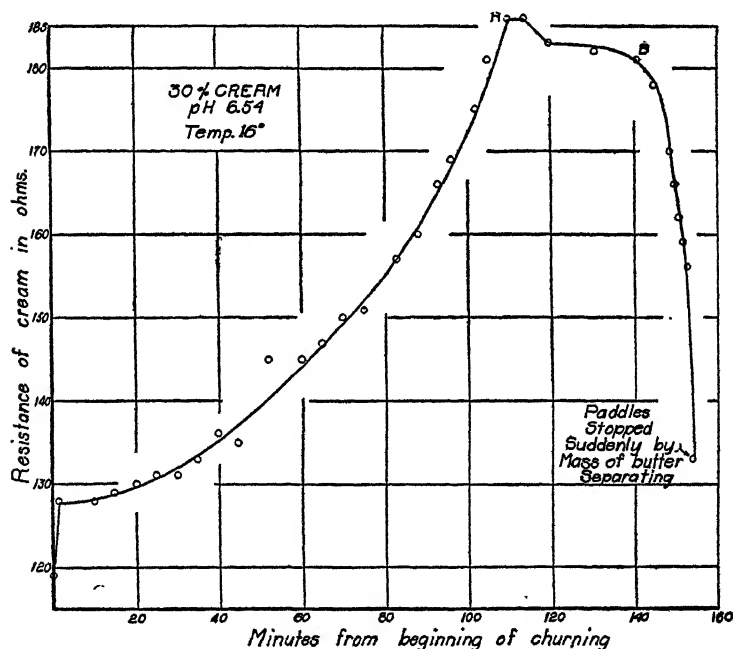


Figure 9.—Change in conductivity of cream during churning.

be grown in a single year, and when that time comes, if not before, colloid chemistry will be called upon to devise some remedy whereby a tropical plantation can be maintained over long periods of time in a high state of productivity.

We read in the narratives of tropical explorers how the natives clear a portion of the jungle, cultivate it for a few years, and then let it grow back to "bush" again, at the same time clearing a new area. I used to wonder at their stupidity but

does not the answer lie in the nature of the soil colloids? In the temperate regions we have alternate freezing and thawing or wetting and drying, which serve to flocculate the colloids of "puddled" soils. All of us have probably seen soils so deflocculated that they baked hard and refused to support plant growth, but the next spring, after a winter of frost, they were again good agricultural land. Heavy soil under intense cultivation is very readily deflocculated and the aborigine probably abandons his cleared area for this reason. Eventually the root growth of trees and bushes, and the burrowing of insects and earth worms does for the tropical soil what frost does in the colder zones.

I have presented a very imperfect outline of colloid chemistry as related to Agriculture. The problems are everywhere, the trained workers are few. We need workers, and can offer, for their reward, the gratitude of future generations.

#### DISCUSSION ON R. A. GORTNER'S PAPER

### THE APPLICATION OF COLLOID CHEMISTRY TO AGRICULTURAL PROBLEMS

CHAS. A. SHULL: Dr. Gortner has given us a very fine presentation of the ways in which colloid chemistry serves agriculture and humanity. There are one or two questions that arose in my mind that I would like a little more information on. I would like to ask in regard to such plants as the cacti as to where these colloidal materials are located in the plants, and what distribution they may have; also I should like to ask in regard to the hardiness of wheat, whether these various types of hardy wheat show that hardiness right from the beginning of life, or whether it is a condition that develops as a result of cold or exposure.

R. A. GORTNER: In regard to the cacti, I must simply say that I do not know. The evidence is that the hydrophilic colloids of the cacti are pentosans. The mechanism in the cacti is different from that in winter wheat although hydrophilic colloids are involved in both, for drouth resistance does not mean cold resistance. Many cacti are very winter tender. It would be extremely important to make sections of large cacti and find out whether the colloidal material is distributed

uniformly throughout the whole plant. In regard to the wheat, I would prefer to have Mr. Newton answer that question.

R. NEWTON: In regard to the wheat, the seedlings in their young stages do not show any difference whatever. This change develops with cold and then they become specific. The hydrophilic colloids in the winter-hardened wheat are apparently proteins and are within the cells, not in the intracellular sap. We have not as yet made a study of their rate of development. That is a problem we hope to attack in the future.

J. ALEXANDER: In connection with flour, I would like to ask whether or not you have determined the various percentages of the various proteins present. Some of those things go into solution more readily than others, and you have a rather complicated system all around. I was wondering whether a similar condition does not exist in wheat gluten to what we find in milk, where one of the differences between mother's milk and cow's milk lies in the protective colloid.

R. A. GORTNER: In regard to the flours that I reported on; in the first place, as far as we could determine protein distribution in the two flours, there are practically no differences which are not within the experimental error of the methods. In the second place we got a tremendous increase in viscosity when we washed the salts out. To our great surprise we obtained our greatest viscosities at the point where practically all the gliadin had been washed out by the distilled water. In other words gliadin is appreciably soluble in distilled water and can be almost completely removed by washing the flour with water. This leaves the glutenin as the only important protein remaining in the flour residue, and it is with this residue that we attain our highest viscosities on the addition of sufficient lactic acid to bring the mixture to a  $p_H$  of 3.0.

Woodman in a recent paper (*J. Agr. Sci.*, 12, 231-243 (1922)) has studied the strong and weak flour question from a different angle and has, from totally different kind of data, reached the conclusion that the glutenin fraction of the proteins is responsible for flour strength.

The question of flour strength does not look like one involving primarily protective colloids but rather the degree of colloidal-ity of the glutenin and the conditions under which the proteins are laid down in the wheat berry determine this point. In



other words we have here a rather extreme instance of the hysteresis or "memory" of an emulsoid gel system.

E. K. CARVER: What proportion of the water is held by the living part of the cell and what by the other? Do these structures lose their hydrophilic properties, and if they do, have you an explanation for that? Why do these cells lose these properties when they are dried.

R. A. GORTNER: I do not know the proportion of the water held by the living protoplasm. The plants lose their winter-hardy condition when warm weather comes or when the plants are dried. That is, the hydrophilic properties disappear. It is probably primarily a question of the colloid structure of the protoplasm.

E. K. CARVER: Is it physical or chemical?

R. A. GORTNER: I believe it is merely a destruction of the colloidal of the protoplasm. That is an unsatisfactory explanation, I know, because it doesn't explain anything. It is simply another way of saying that the scientific bases underlying the phenomenon are unknown.

E. K. CARVER: You can grind the fresh leaves and get your colloids just the same.

R. A. GORTNER: Yes.

J. ALEXANDER: They had a very large number of very valuable papers, including one by Dr. Shull, on soils, in the *Transactions of the Faraday Society* about a year ago (17, 217-399 (1922)). They had a big symposium on this general topic. The meeting was presided over by Sir A. D. Hall.

R. NEWTON: As to whether the change is a physical or a chemical change, I believe it is probably a physical and not a chemical change. Possibly most of you have seen a paper by Chibnall, *Biochem. J.*, 16, 599-607 (1922), on the effect of low temperature drying on proteins in leaves and the fact that the low temperature drying at 40 degrees had no effect whatever on the chemical distribution but it had a great effect on the physical dispersion.

A VOICE: I would like to display my ignorance: Some years ago at the flour mill we had a very dry summer, so dry that our wheat was so dry that it was difficult to mill it, never-

theless the wheat showed a remarkable tendency to heat in the bins. I would like to have some explanation of that from Dr. Gortner.

R. A. GORTNER: I cannot explain it.

THE VOICE: We had to turn out the bins almost every day.

R. A. GORTNER: I would like to ask if the drouth was so severe that the wheat was badly shriveled?

THE VOICE: Yes. The wheat was quite badly shriveled.

R. A. GORTNER: Then the explanation of the heating probably lies in the shriveled condition. Dr. Bailey has shown that in shriveled wheat there is a much greater reduction in the amount of endosperm than in the weight of the embryo, and that the actively respiring portion of the wheat berry is the embryo. Therefore in a given weight or volume of shriveled wheat you have a large increase in the actively respiring tissues with a corresponding increase in heat production. The heating plant is out of all proportion to the size of the house. Shriveled wheat should therefore be expected to heat at a lower moisture content that would be the case for plump wheat.

R. THIESSEN: In regard to the expressibility of water from colloids, there is a remarkable example of that in peat. That is a typical colloid and the peat manufacturers are trying to press water out of the peat, but it cannot be done. But when peat freezes, the water will run out itself.

J. ALEXANDER: The same thing happens with glue.

(COMMUNICATED DISCUSSION)

R. A. GORTNER: Certain of our observations on flour proteins apparently throw evidence on the question as to whether or not the swelling of proteins is a colloidal or a purely chemical phenomenon. When the salts have been leached from a sample of wheat flour, and incidentally most of the gliadin had been removed, it has been possible by the addition of lactic acid to increase the viscosity from 4° MacMichael to 456° MacMichael. If, however, alcohol has been used at any stage in the process the maximum viscosity attainable with lactic acid is very much lower, *e. g.*, 202°, 160°, or 105° Mac-

Michael instead of 456° where no alcohol had been used. Merely doughing up a flour with alcohol, removing all of the alcohol by evaporation before an electric fan and then attempting to make bread or carrying out viscosity measurements on the flour which has been so treated shows that the tenacity of the gluten and the *hydration or swelling capacity of the proteins has been destroyed*.

In such an instance the differences in swelling are certainly not hydrogen ion effects nor can I see how they can be due to chemical factors. The colloidalilty (the degree of dispersion) of the system has been changed from near a "maximum zone of colloidalilty" to a point where colloidal effects are less pronounced. This behavior of the flour protein is an excellent example of what I regard as the colloidal behavior of a protein system as contrasted with stoichiometrical chemical reactions.

F. E. BARTELL: If there are no further discussions or questions on this paper, we will close this First National Symposium on Colloid Chemistry. Dr. Mathews was suddenly called away and he will not be here to bid us farewell, but he asks me to state that this terminates the Symposium and to bid you farewell in his behalf, and he hopes that we may all meet together next year at Northwestern University.

(Prolonged applause and cheers)

DR. HOLMES (CHAIRMAN): The chair will now entertain a motion expressing the appreciation of this body to Dr. Mathews for his fine work and leadership in carrying out this symposium and for the fine support of this department and this University. Let me state also, in better justice to Dr. Mathews, that although the Colloid Committee of the National Research Council had endorsed this idea and coöperated in the work, it was Dr. Mathews' idea originally to hold such a symposium, and by far the major part of the credit for carrying out this symposium idea is due to him.

R. A. GORTNER: I usually hold my ear pretty close to the ground, and this whole idea of a symposium was summed up for me last night on the porch of the University Club, where we were discussing the importance of a symposium of this kind as compared to the old-time way of gathering and holding meetings, in the statement that in the one case you had a "department store" and in the other case you had a "five-and-ten-cent store," and I would like to introduce a motion of appreciation from the Colloid Symposium and all the members who are present, to Professor Mathews, Professor Svedberg, to the members of the staff of the Department of Chemistry, to the University of Wisconsin, and to the State of Wisconsin for the opportunity given us to come here and sit down around a table, as we virtually have done, and discuss our problems together.

(Motion received several seconds)

R. THIESSEN: Let me just say that this has been one of the most fascinating meetings to me that I have ever attended. I am in the habit of attending the regular meetings of the chemical societies, but I have never gotten as much good, in fact I have gotten more good out of this meeting than I have out of a great number of the meetings of these societies put together. When I heard that this symposium was to be held here, I made up my mind that that was the one place where I wanted to go. I began to study colloid chemistry years ago when Ostwald first began his talks on colloid chemistry, and I concluded that there must be something in it in order to explain all these things that could in no other way be explained. I do not say that colloid chemistry is the panacea for everything, but it does clear up many mysteries. This has been the most interesting meeting I have ever attended in my life, and this is just a scratch on the surface compared to what we are going to do. Dr. Mathews is certainly to be congratulated on this splendid accomplishment, and for getting these men together in order to make plans for future meetings, for let not this be the only meeting, but let us meet again and again and again, for we can no longer be without these meetings.

(Prolonged applause)

DR. HOLMES: All those in favor of the motion which has

been put will please vote aye, and those contrary-minded vote no.

(Ayes)

DR. HOLMES: Unanimous.

J. H. MATHEWS: I assure you that I feel well repaid by this remarkable demonstration, not only this morning but by your good attendance and by the many kindnesses that you have shown me during the week. I think this is a very auspicious time to read a letter which I received by personal messenger from the President of the Northwestern University this morning. This letter reads as follows:

*"My dear Professor Mathews:*

I would very greatly appreciate it if you would be so good as to extend to the National Symposium on Colloid Chemistry a most hearty invitation from Northwestern University to come to Evanston for your June meeting in 1924.

We believe that Evanston would be a convenient and comfortable place for your meeting and we can assure you here a most hearty welcome.

Yours truly,

Signed: WALTER DILL SCOTT."

I also had delivered to me, by the same messenger, a Resolution which was passed by the Chicago Section of the American Chemical Society last evening and which is signed by Carl S. Miner, Chairman, reading as follows:

*"Resolved* that the Chicago Section strongly favors holding the second National Symposium on Colloid Chemistry at Northwestern University and pledges its support in case the invitation of that institution is accepted.

Signed: CARL S. MINER,

*Chairman"*

As I told you a day or two ago, the Colloid Committee of the National Research Council, has voted unanimously to have another Colloid Symposium next year. Although this First Symposium was more or less a spontaneous sort of affair, I think that we should have some organization hereafter to father this institution, and I know of no better body than the Colloid Committee of the National Research Council for that job, so

we will leave the matter of the acceptance of this invitation to the determination of the Colloid Committee of the National Research Council.\*

(Prolonged applause)

DR. WHITMORE: First of all, ladies and gentlemen, I want to assure you that we will do our level best at Northwestern, and we have the promised assistance of the Chicago Section to live up to the glorious example which has been set up here.

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\* Footnote: By unanimous vote the Colloid Committee of the National Research Council accepted the invitation extended by Northwestern University.



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